TEXTILE RESEARCH JOURNAL

Publication of

TEXTILE RESEARCH INSTITUTE

VOLUME XXVIII SEPTEMBER 1958 NUMBER 9

file these fibers under today

Rhovyl-55 and Rhovyl-T the first family of vinyl fibers, production- and wear-proven for years, to meet tomorrow's competitive challenge

some facts for comparison:

shrinkage: Thermally treated Rhovyl-T won't shrink—but look: Rhovyl-55 shrinks **evenly** up to 55%! Unsurpassed for suedes, carpeting, furs, dimensional effects.

strength: 2.7-3.0 g./d. for Rhovyl-55, and 1.0 g./d. for Rhovyl-T wet **or** dry. High abrasion resistance and elastic recovery.

care-free: Does not absorb water, does not swell: hence, it's quick-drying, crease-resistant, needs no ironing.

chemical resistance: Unaffected by virtually all acids, bases, oxidants. Won't mold or deteriorate. Resistant to sun and sea. For filters, work clothes, military equipment.

noninflammable: Safer for apparel, carpeting, upholstery, Rhovyl can't burn.

colorful: Staples available in pure white and 20 dope-dyed colors —easily dyed with acetate, naphthol and indigosols, too.

WRITE OR PHONE TODAY for more information on what polyvinyl chloride Rhovyl® staple fibers can do for you.

RHOVYL

RHODIA INC., 60 East 56th Street
New York 22, N. Y. (Phone: PLaza 3-4850)

TEXTILE RESEARCH JOURNAL

VOL. XXVIII *September 1958* NUMBER 9

Editor: **Julian S. Jacobs**

Production Editor: **Candida Frenking**

Advisory Board

H. J. Ball
Earl E. Berkley
Henry Eyring
W. J. Hamburger
Milton Harris
K. L. Hertel
Harold P. Lundgren
H. Mark
E. R. Schwarz

TEXTILE RESEARCH JOURNAL, published monthly at Prince and Lemon Streets, Lancaster, Pa., is devoted to the interest of research in textile and allied industries. It is published by Textile Research Institute.

Entered as second-class matter, April 27, 1945, at the post office at Lancaster, Pa., under the Act of August 24, 1912. Accepted for mailing at special rate of postage provided for in paragraph (d-2), Section 34.40, P. L. & R. of 1948, authorized May 9, 1950.

Manuscripts and communications should be sent to the Publications Department, P.O. Box 625, Princeton, N. J.

Subscription rates: $20.00 per year; additional for postage, 50 cents to Canada, $1.00 to all other countries. Single copies, $2.00 each.

Contents copyrighted © 1958 by Textile Research Institute. Advertising rates supplied on request.

IN THIS ISSUE

Evaluating Antistatic Finishes. *Fred H. Steiger* 721

Structural Compactness of Woven Wool Fabrics and Their Behavior in Modern Washing Machines. *Herman Bogaty, George H. Lourigan, and Hazel E. Harris* 733

Cyanoethylation of Cotton in Aqueous Medium. *Norbert M. Bikales and Lorence Rapoport* 737

A Method for Determining the Sulfur Content of Wool. *M. V. Glynn* 744

Papers Presented
28th TRI Annual Meeting

Predicting Commercial Acceptance of a Fiber. *J. L. Barach, R. G. Stoll, and A. F. Tesi* 747

Recent Advances in the Industrial Use of Synthetic Fibers. *J. M. Swanson* 755

Recent Developments in Lofted Acetate Yarns for Apparel and Home Furnishing Fabrics. *R. E. Semmler, R. F. Dyer, R. C. Forrester, and W. G. Faw*

Part I: Apparel Fabrics 761
Part II: Lofted Carpet Yarns 765

Chemical Modification of Cotton: Progress and Current Status. *C. H. Fisher and F. S. Perkerson* 769

Some Concepts of Cotton Research. *George S. Buck, Jr.* ... 778

Ultraviolet Absorbers. *R. A. Coleman and W. H. Peacock* .. 784

Whither Rayon? *John Wharton and G. V. Lund* 792

On the Physical Properties of Rayon and Nylon 66 Tire Cords at Elevated Temperature. *Frank R. Charles and Clement Tarzi* 797

Non-Apparel Applications of Viscose Rayon. *John A. Howsmon* 805

LETTERS TO THE EDITOR

An Application of the Davidson Color Matching Method. *F. Bryant* 811

Isolation and Identification of Fumaric Acid in Raw Cotton Fiber. *Luis E. Gregory and George V. Merola* 813

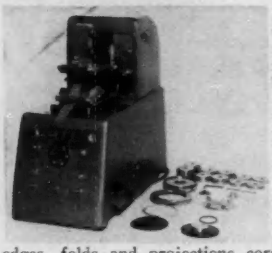
Improvement on the Servo Conversion of Manual Fibrographs. *John D. Tallant* 815

Book Reviews 816

Announcement: Conference on Military Applications of Fabrics for Coating 818

REPRINT REQUESTS SHOULD BE DIRECTED TO THE AUTHORS
SEE ARTICLES FOR ADDRESSES

ABRASION TESTER



Exhaustive studies show that resistance to service wear cannot be satisfactorily characterized by surface abrasion data alone or by such characteristics as tensile and tearing strength. However, the weighted consideration of the resistance to abrasion by flexing and bending, surface abrasion of flat areas, and abrasion of edges, folds and projections correlate significantly with the actual wear resistance. The CSI Stoll Quartermaster Universal Wear Tester is a multipurpose instrument for measuring resistance to laboratory wear (as stated above) of such materials as woven and knitted fabrics, napped and pile fabrics, hosiery, felt, non-woven and coated fabrics, yarns, threads and cordage, plastic films, rubber sheeting, leather, paper and many other materials.

ASTM Designations:
D1175-55T "Test for Abrasion Resistance of Textile Fabrics."
D1379-55T "Test for Abrasion Resistance of Textile Yarns."
D1375-55T "Test for Pilling Propensity of Textile Fabrics."

Federal Specifications:
CCC-T-191-b Method No. 5300.
CCC-T-191-b Method No. 5302.

As our name implies we also welcome the opportunity to work on custom design and manufacture of testing instruments of all types for individual and general needs.

CUSTOM SCIENTIFIC INSTRUMENTS, INC.
541 Devon Street *Kearney, New Jersey*

ACADEMIC PRESS BOOKS

Inorganic Fibres

By C. Z. CARROLL-PORCZYNSKI
Director of Textile Research, British Belting and Research Company, Ltd.

September 1958, 353 pp., illus., $11.00

CONTENTS:

Glass Fibres. Glass Textiles. Glass Textiles in the Electrical Industry. Glass Reinforced Plastics. Glass Wool. Slag Wool. Rock Wools. Refractory Fibres. Asbestos. Asbestos in the Plastics Industry. Asbestos in the Electrical Industry. Other Industrial Applications of Asbestos. Recent Developments in the Asbestos Industry. Inorganic Fibre Papers. Wire Weaving. Knitting. Metal Wool. Metallic and Metallized Yarns. Metallized Fabrics. APPENDIX. INDEX.

Fibres, Plastics, and Rubbers

A Handbook of Common Polymers

By W. J. ROFF
British Cotton Industry Research Association

1956, 400 pp., illus., $10.00

CONTENTS:

PART I. LIST OF DATA ON INDIVIDUAL POLYMERS: Structure. Chemistry. Physics. Serviceability and Utilization. History. Additional Notes. Additional References.

PART II. LIST OF TABLES ON INDIVIDUAL POLYMERS: Carbohydrate Condensation-type Polymers. α-Amino-Acid Condensation Polymers (Proteins). Synthetic Linear Condensation Polymers (Polyamides and Polyesters). Linear Addition Polymers (Hydrocarbon and Vinyltype Polymers). Cross-linking Polymers. Organo-silicon Polymers. Miscellaneous Inorganic Polymers.

PART III. LIST OF TABLES ON SPECIFIC PROPERTIES AND RELATED INFORMATION: Structure. Chemistry. Physics. Serviceability and Utilization. History. Additional References. INDEX.

Complete in 3 volumes

Rheology

Theory and Applications

Edited by FREDERICK R. EIRICH
Polytechnic Institute of Brooklyn

THIS LUCID, AUTHORITATIVE treatise presents a condensation of facts and theories on a variety of topics ranging from metallurgy, plastics, and glasses to rubbers, fibers, gels, ceramics, inks, solutions, and pastes. Two volumes of this three-volume work have been published; Volume 3 is in preparation.

Descriptive literature available upon request

ACADEMIC PRESS INC.
PUBLISHERS
111 Fifth Avenue, New York 3, New York

SEPTEMBER 1958
VOL. XXVII NO. 9

TEXTILE RESEARCH JOURNAL

Evaluating Antistatic Finishes

Fred H. Steiger

Rohm & Haas Co., Philadelphia, Pa.

Abstract

Following a brief summary of the published methods for the measurement of static electricity on textiles, the effect of test variables is explored. The relations between charge, resistivity, and the concentration of the antistatic finish are investigated, and it is demonstrated that on a given fabric the logarithm of the charge is a linear function of the logarithm of the surface resistivity, independent of the finish which produces the electrical conductivity.

Test Methods

Many methods for measuring the static electrification of materials have been proposed. These tests vary as to the means of inducing a charge as well as in their method of determining the quantity of charge generated.

For example, the charge may be generated by rubbing the sample with a rubber or Neoprene gloved hand [24, 40], a piece of cloth [28], or a rigid bar or disc [29, 35, 38]. The sample may be passed through rollers alone [8, 22, 30] or as the center of a sandwich of plates [19]. Electrification may be produced by sliding the sample down an inclined plane [9] or by rolling a ball down the sample [16]. The material being tested may be touched by a spring-loaded plunger [15, 23], stroked by filaments [21, 25], rubbed by a metal plate or wheel [6, 34], or moved past stationary bars and guides [2, 3, 10, 13, 17, 23, 32]. Contact with mercury also has been employed as a means of building up an electrical charge [31].

The charge which is generated could be measured in terms of an effect which it produces, such as repulsion of similarly charged surfaces [37]. Generally, however, the charge or voltage itself is measured. The most common means of measurement involves a Faraday Pail, by which the charged sample or rubbing surface is placed in a metallic container insulated from the surroundings. The charge induced on the container by the presence of the charged body then is measured by a suitable means [8, 9, 16, 19, 22, 23, 24, 35, 40].

The charge on the electrified sample also may be measured directly [21, 25, 29, 30, 32, 35], through the medium of a corona brush [2, 6], or by virtue of a potential induced by movement of the charged sample with respect to a reference material [3, 15, 17, 23], or by movement of the reference object with respect to the fabric. Several workers have chosen to measure the electrification of the rubbing medium, since this is equal in magnitude but opposite in sign to the charge on the sample [10, 13, 31, 34].

It has been observed that static electricity manifests itself primarily on materials which are poor electrical conductors. Consequently, many workers have proposed resistivity tests as a measure of the tendency of materials to accumulate static electricity [1, 7, 13, 18, 22, 32, 39, 40]. Grüner [14] has reported that an antistatic agent of unspecified composition has little effect on contact potential; its effectiveness is attributed to decreased resistivity. Since it is not possible to determine the distribution of conductive paths over fabric, McLean [27] has criticized resistance measurements for the evaluation of the static electrification of textiles.

As Silsbee [36] points out, high resistance can be measured by determining the rate at which a charge initially in a capacitance, C farads, will leak away through a resistance, R ohms, which shunts the capacitor. If the time to go from the initial potential, V_1 volts, to the final potential, V_2 volts, is t seconds, then

$$R = \frac{0.43\,t}{C\,(\log V_1 - \log V_2)} \qquad (1)$$

Thus a comparison of the rates of decay of electrical charges is a comparison of resistances, provided the capacity of the system remains constant. Several workers have used this charge decay method to measure the resistance of fibers, yarns, and fabrics [2, 12, 22, 33].

Other means of measuring the high resistance involved also have been employed [7, 18, 20, 39].

In this investigation the Electrical Resistance Tester, made by Custom Scientific Instrument Company and employing the circuit described by Hayek and Chromey [18], was used. Because the values generally were greater than 10^6, surface resistivities are reported as the logarithm of the ohms per square of fabric. This method of testing and reporting is in accordance with AATCC Tentative Test Method 76-54 [1].

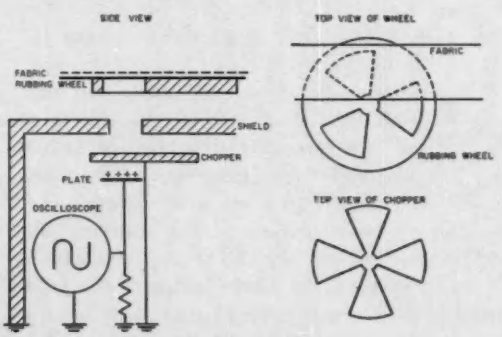


Fig. 1. Schematic representation of static electricity measuring device.

A second test was constructed in our laboratory to measure the static charge built up on a fabric. The unit is similar to instruments described by Havenhill, O'Brien, and Rankin [15] and by Ballou [3].

As indicated in Figure 1, the electrified fabric induces a charge of opposite sign on the plate. When the blade of the grounded chopper interposes itself between the fabric and the plate, the charge returns to the ground. The charge on the plate reappears when the blade has passed. Thus an alternating current which can be measured by an oscilloscope is set up in the ground lead of the plate.

To generate a charge on the fabric, a wheel, similar in principle to the chopper in the detecting unit, was mounted outside of the shielded unit, concentric with the chopper and as close to the top of the detecting unit as was practical. The fabric was drawn over half of the wheel and was held at constant tension on the top surface of the wheel. As the wheel rotated, it rubbed the underside of the fabric. When an opening in the wheel was reached, the fabric was exposed to the detecting unit below.

The speeds and number of blades of the chopper and of the wheel were chosen so that it would not be possible for exposures and readings to become synchronized. This precaution was necessary, since readings consistently made when the fabric was partially or completely covered by the rubbing wheel would lead to erroneously low values.

Oscilloscope tracings were difficult to read because of fluctuations produced by the nonsynchronous arrangement. To overcome this, readings were made at a high sweep frequency, where all tracings were merged into a solid band. The readings of interest to us were the maximum and minimum tracings, which defined the width of the band.

To calibrate the instrument for the present study, an insulated metal plate was placed above the detecting unit at the same distance at which the fabric is held during testing. This necessitated removing the external rubbing wheel. The plate, which is somewhat larger than the opening of the detecting unit, was charged to a known voltage by a series of "B" batteries, and a reading of the band width on the oscilloscope was made. The number of volts

per unit scale reading divided by the area of the opening in the detector unit provided the constant necessary to convert readings to volts per unit area of fabric.

To convert the voltage readings to average charge on the fabric, the capacity of the test instrument was determined by measuring the rate of voltage loss when the charged calibration plate was grounded through a 1.00×10^{13}-ohm resistor. From Equation 1 the capacity of the unit was found to be 8.4 micromicrofarads. This value was employed in converting all voltage readings to charge.

To prepare fabric for testing, Type 200 nylon taffeta, 70-den. 34-filament, was scoured in 0.02% Triton X-100 and rinsed completely free of detergent, then air-dried. Portions of this fabric were padded two dips and two nips through various baths. Applied solids on the fabric were assumed to be a fixed percentage of the solids in the bath. The percentage (the wet pick-up of the fabric) was determined by measuring the weight gain of the fabric immediately after a typical padding operation. Samples were conditioned for at least 16 hr. in the atmosphere in which they were tested. Unless otherwise noted, measurements were made in a room at 70° F. and 65% relative humidity.

Test Variables

Nature of the Surfaces

The identity of the surfaces in contact has a marked effect on the amount of static electricity which is generated. Preliminary work indicated that aluminum generates large charges against a number of fabrics; consequently the rubbing wheel was made from this metal. The grounded rubbing surface was kept constant throughout this study.

To select a material for this study, several different fabrics were tested. The values of charge in Table I were obtained against the aluminum wheel after 1 min. of rubbing.

Nylon was chosen for further study because the high charge value on the untreated fabric permitted the effect of finishes to be seen most readily.

Tension and Pressure

The fabric is clamped in a bar, then laid over the external rubbing wheel and over a second bar. In order for the fabric to make firm contact with the wheel, the bars are maintained about ¼ in. below the top level of the wheel. A weight is clamped to the free end of the fabric to hold it in place during the testing. The amount of weight, therefore, affects the tension in the warp yarns which pass from clamp to weight and affects the pressure of the fabric against the wheel.

TABLE I. Static Charge on Various Fabrics

Fabric	Charge, $\mu\mu C/cm.^2$*
Nylon—Type 200, taffeta	5200
Orlon†—Type 81, plain weave	1200
Acetate—Bright filament, taffeta	770
Arnel—Filament, taffeta	500
Dacron†—Filament, ribbed shirting	360
Cotton—Print cloth	

* $\mu\mu C$ = Micromicrocoulombs.
† Du Pont trademark.

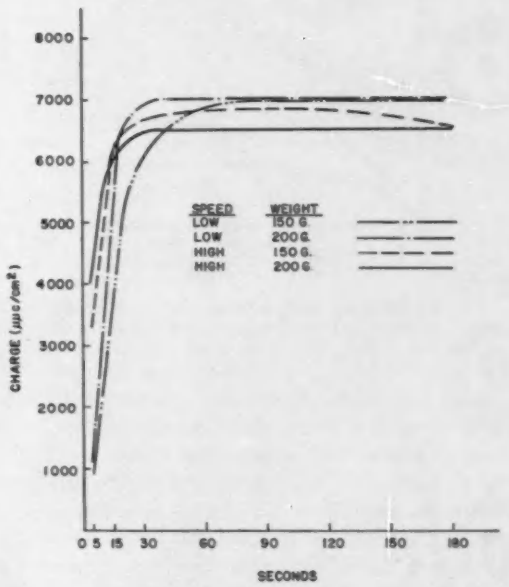


Fig. 2. Effect of rubbing speed and clamp weight on the charge generated on untreated nylon.

Untreated nylon and nylon treated with two concentrations of two typical antistatic agents then were tested to determine the effect of clamp weight on the charge generated. The results are indicated in Figures 2–6.

Speed of Rubbing

Götze, Brasseler, and Hilgers [11] showed that the amount of charge on yarns of different types increases with speed. Working with automobile tires, Liska and Hansom [26] found the same effect.

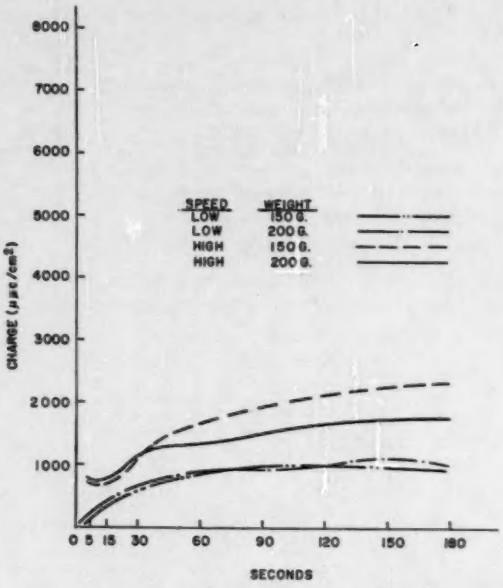


Fig. 3. Effect of rubbing speed and clamp weight on the charge generated on nylon treated with 0.07% applied solids of Agent A.

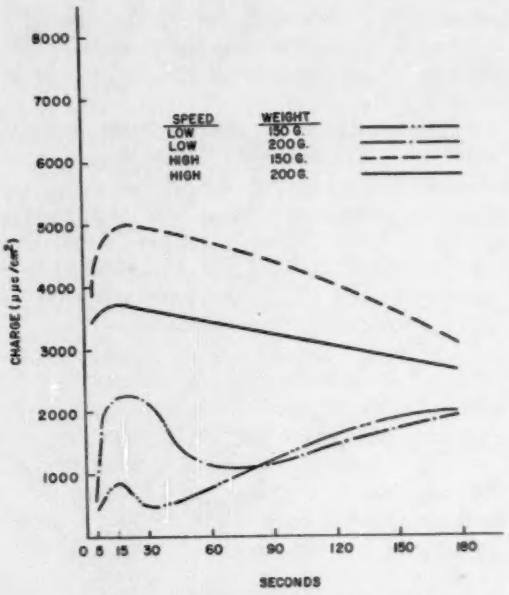


Fig. 4. Effect of rubbing speed and clamp weight on the charge generated on nylon treated with 0.03% applied solids of Agent A.

Bulgin [4] stated that voltage increases with speed on tires of low electrical resistance, but with high resistance tires the voltages tend towards a limiting value. Gonsalves and van Dongeren [10] also noted that with some fibers the charge is independent of rubbing velocity. The presence of an electrically conductive finish accounted for those cases where dependence on velocity was observed.

Working with nylon and wool on metals, Medley [29] noted a constant upper limit of charge that was independent of rubbing speed or humidity below 70% RH. At higher humidities slow speeds produced lower charges than high speeds.

Hersh and Montgomery [21] stated that when an insulator and a metal are rubbed together, the amount of charge increases linearly with velocity until a limiting value is reached. In insulator–insulator systems except those involving Teflon, the charge is independent of velocity. Later Levy and Dillon [25] found a velocity effect in insulator–insulator systems.

All these cases suggest that electrical resistivity is the factor which controls the dependence of charge on velocity. It may operate as given below.

When the resistance is low, the rate of charge leakage is high. In that case, if the rate of charge generation increases as the velocity increases, there is a net gain in total charge on the fabric. The charge on the fabric then is a function of the velocity of rubbing. At high resistances, however, low rates of charging can saturate the system. Increasing the velocity in this case has little effect on the total charge.

To determine the magnitude of the effect of velocity in our experimental equipment, the untreated and treated nylon referred to in the previous section were tested at 1800 r.p.m. and approximately 600 r.p.m. The charge readings are indicated in Figures 2–6 as a function of time of rubbing, another variable in the test.

The velocity effect is as predicted. Only treated samples show a significant increase of charge with velocity.

At the higher speed the 200-g. weight generally produces lower charges than the 150-g. weight. The reverse may be true at the lower speed. Since the weight may affect the actual speed of rubbing, these conclusions are tentative. For test purposes the 200-g. weight and 1800 r.p.m. were chosen arbitrarily.

Figure 2 indicates that the charge on untreated nylon rises to a maximum value and remains at this

level. Treated nylon, however, shows a maximum generally followed by a decline in charge on prolonged rubbing. This probably is due to the transfer of antistatic finish to the wheel.

Attempts to eliminate agent transfer by cleaning the wheel during testing by pressing a clean cotton cloth to the wheel produced excessive heating, which naturally had an effect on the condition of the fabric being tested. Therefore, the cleaning procedure was discontinued and the wheel was cleaned thoroughly only between tests. The pressure on the fabric being tested was not the same as that which was exerted on the cleaning cloth; consequently heating due to friction of the test sample was not as great.

Time of Rubbing

It is the change which continued rubbing produces on fibers covered with a few surface layers of antistatic agent which makes selection of a test end-point difficult. As is illustrated in Figures 2–6, only untreated nylon reaches a true equilibrium value. The other curves have a maximum as a common feature.

To investigate the effect of time of rubbing, nylon samples treated with several antistatic agents of varying concentration were tested. Figures 7 and 8

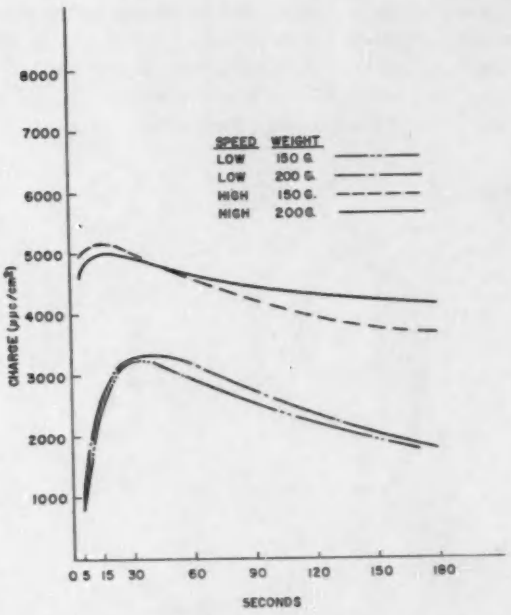


Fig. 6. Effect of rubbing speed and clamp weight on the charge generated on nylon treated with 0.08% applied solids of Agent B.

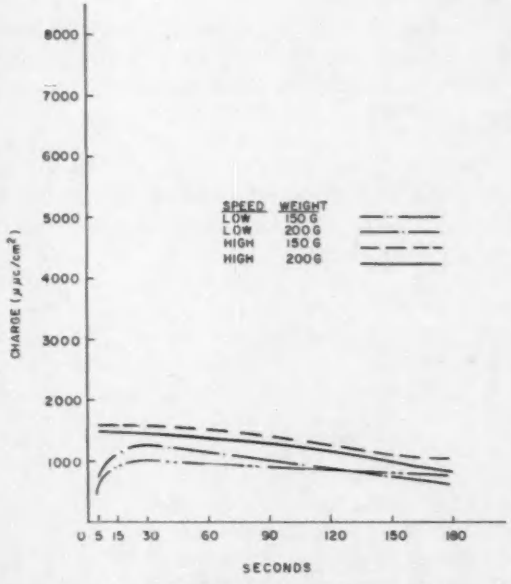


Fig. 5. Effect of rubbing speed and clamp weight on the charge generated on nylon treated with 0.17% applied solids of Agent B.

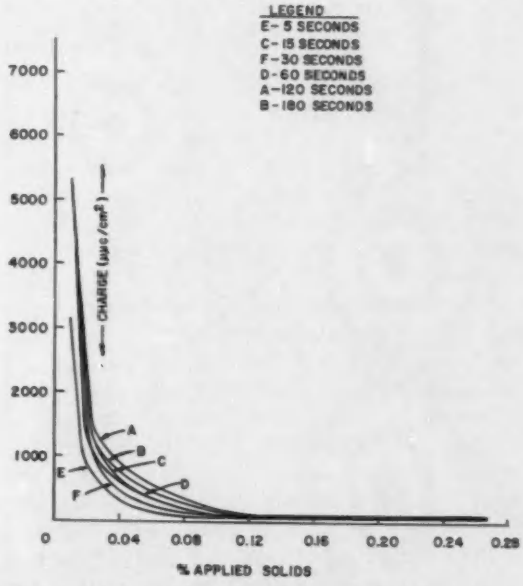


Fig. 7. Effect of Agent A on nylon rubbed for various lengths of time.

show that the variations due to time of rubbing are small compared to the changes produced by the antistatic agents. It should be noted that these figures are plotted with different abscissas because of the different efficiencies of the finishes.

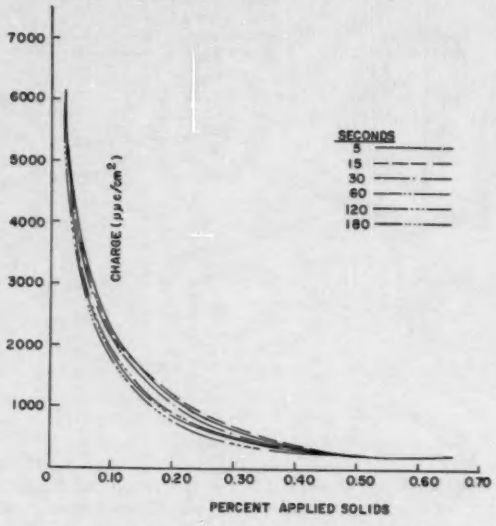


Fig. 8. Effect of Agent B on nylon rubbed for various lengths of time.

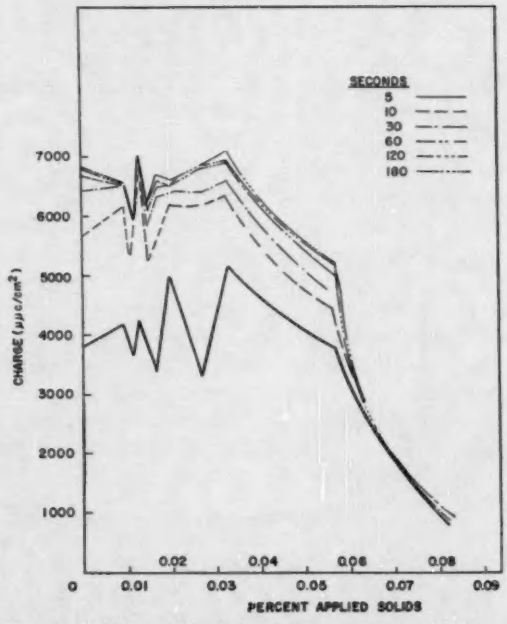


Fig. 9. Effect of alkyl trimethyl ammonium chloride on nylon rubbed for various lengths of time.

In Figure 9, the same study is made of a very efficient antistatic agent at extremely low concentrations. The oscillations of the curve will be discussed later. For the present we may note that, except for the curve derived from values determined at 5 sec. of rubbing, most of the curves lie within ± 5% of an average curve. Even the curve from the lowest time has the same general shape as the others.

Figure 2 illustrated the rise of the charge on untreated nylon. Under the test conditions it took somewhat less than 60 sec. to attain equilibrium. Since results at 1 min. are in general agreement with all other results, this time was settled on as standard for the test.

Nature of Antistatic Finishes

In order to learn about the contribution of chemical types, three antistatic agents of dissimilar chemical structure were employed for further study. These materials were:

Agent A—dialkyl dimethyl ammonium chloride
Agent B—alkylphenoxy polyethoxy ethanol
Agent D—alkyl alkanolamine phosphate

Discussion

Resistivity

The data of Table II plotted in Figure 10 show that the logarithm of resistivity is a straight line function of the logarithm of applied solids.

Charge

Figures 7 and 8 appear hyperbolic. If this is true, a plot of charge versus the reciprocal of the percent

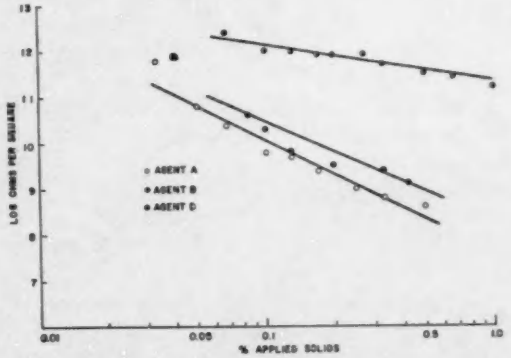


Fig. 10. Relations between the logarithm of resistivity and the logarithm of concentration of applied antistatic agent.

TABLE II. Effect of Concentration of Antistatic Agents

Applied solids	Resistivity, log ohms/square	Charge, $\mu\mu C/cm.^2$	Applied solids	Resistivity, log ohms/square	Charge, $\mu\mu C/cm.^2$
	Agent A		0.067	12.4	1900
0.50	8.6	36	0.050	13.2+	2200
0.33	8.8	45	0.033	13.2+	5000
0.25	9.0	68	0.030	13.2+	5400
0.17	9.4	72	0.027	13.2+	3600
0.13	9.7	160	0.025	13.2+	4300
0.10	9.8	120	0.023	13.2+	5600
0.067	10.4	220	0.022	13.2+	4500
0.050	10.8	250	0.020	13.2+	4500
0.040	11.9	810	0.018	13.2+	3800
0.033	11.8	680	0.017	13.2+	6800
0.020	13.2+	1300	0.015	13.2+	6300
0.017	13.2+	2200	0.013	13.2+	7200
0.013	13.2+	920			
0.012	13.2+	2200		Agent D	
0.010	13.2+	4300			
0.0090	13.2+	3800	0.42	9.1	63
0.0080	13.2+	5400	0.33	9.4	86
0.0067	13.2+	5400	0.20	9.5	170
0.0053	13.2+	6300	0.13	9.8	290
0.0047	13.2+	6300	0.10	10.3	380
0.0033	13.2+	6100	0.083	10.6	540
			0.067	11.3	810
	Agent B		0.050	13.2+	7400
			0.043	13.2+	7200
1.00	11.2	320	0.040	13.2+	7400
0.67	11.4	360	0.033	13.2+	6800
0.50	11.5	450	0.027	13.2+	7000
0.33	11.7	950	0.020	13.2+	7200
0.27	11.9	1200	0.017	13.2+	6800
0.20	11.9	1500	0.013	13.2+	7200
0.17	12.0	1900			
0.13	12.0	2000			
0.10	12.0	2000	Scoured nylon	13.2+	7000

applied solids should be linear. The data of Table II, however, plotted in Figure 11, show that the situation is not quite this simple.

In the range of practical interest—from values of charge of untreated nylon to about one-tenth of this maximum—the straight line relation holds. At the extremes of the charge–reciprocal concentration curve, deviation from linearity occurs.

Agent D provides data only for the regions which deviate from linearity. While these regions in Figure 11 have been connected by a straight line, a discontinuity in the curve also is a possibility.

Orientation Effects

A periodic fluctuation of charge in the region near the limiting charge is to be noted in some cases as the applied solids of the antistatic agent decrease. The phenomenon can be seen in Figure 9, which is a small section of a charge–concentration curve, as well as in Figure 11 (Agent D), a charge–reciprocal concentration curve.

When Graham [13] plotted static voltage versus applied solids, he obtained two types of curves. For surface-inactive materials, the curve was smooth. The curve for surface-active antistatic agents at low concentrations showed marked periodicity. These alterations were attributed by Graham to the influence of oriented dipoles in rigid monomolecular layers.

Graham's division into surface-active and surface-inactive groups does not cover all cases, since Agent A (Figures 7 and 11) is a surface-active material which lowers surface tension, wets, etc., and yet does not show any marked periodicity of charge. The feature which determines whether the curve will be smooth or not probably is the symmetry of the surface-active compound. Figures 7 and 11 (Agent A), which present data on a dialkyl dimethyl ammonium chloride compound, do not have the inflections which a monoalkyl trimethyl ammonium chloride compound presents in Figure 9. Figures 9 and 11 (Agent D) illustrate the relation between these

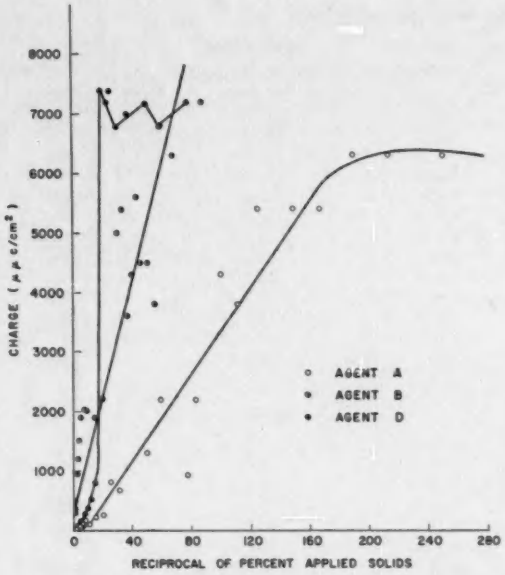


Fig. 11. Relation between the logarithm of charge and reciprocal concentration of applied antistatic agents.

inflections and the amount of antistatic agent present on the fabric.

As Graham suggested, oriented monomolecular layers probably are responsible for the recurring peaks. For one thing, the average quantity of finish required to go from a peak to a valley is approximately the quantity required for a monomolecular layer. This is in agreement with Graham's work. Furthermore, it is easier to conceive of oriented molecular layers in the case of unsymmetrical surface compounds than it is in the case of symmetrical materials. Figure 9 also shows that inversion of peaks can take place on prolonged rubbing. This must be due to the abrasion of molecular layers.

Relation of Charge and Resistivity

Charge and resistivity *in the range of practical interest* have been expressed above as linear functions of the concentration of applied antistatic finish. It therefore is possible to write the following relationships:

$$\log R = -m \log A + B \qquad (2)$$

$$Q = \frac{n}{A} + D \qquad (3)$$

R is resistivity, Q is average charge, A is concentration of applied antistatic agent, and m, n, B, and D are equation constants. From the two equations above the following relation may be derived:

$$\log (Q - D) = \frac{1}{m} \log R + \left(\log n - \frac{B}{m}\right) \qquad (4)$$

In Equation 3, D represents a quantity small compared to the charges in which there is the most interest. Therefore, for practical purposes D may be omitted:

$$\log Q = \frac{1}{m} \log R + \left(\log n - \frac{B}{m}\right) \qquad (5)$$

Figure 12 presents graphs of the data in Table II where both charge and resistance values are available. According to calculations of the 95% confidence limits, there is no significant difference between Agents A and D in the entire range investigated. Readings for Agent B were not obtained below a resistance of 11.2. Above this resistance value the curve for Agent B overlaps considerable portions of the other curves.

To further test these equations, data were obtained at two relative humidity levels for nylon treated with four concentrations of nine different antistatic agents. Figures 13–18 are plots of this data made according to Equations 2, 3, and 5.

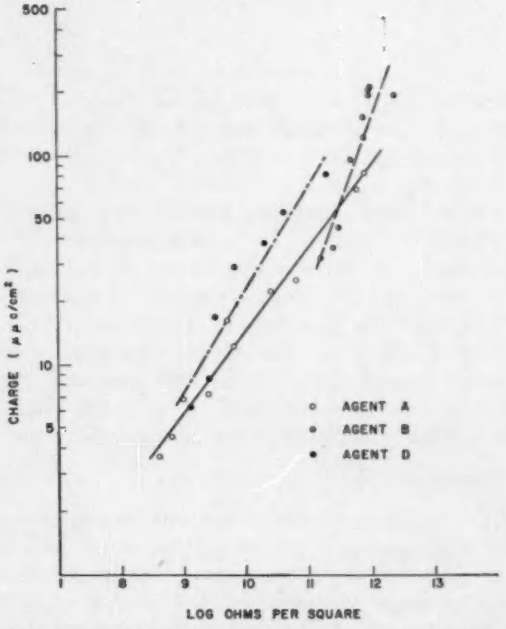


Fig. 12. Relation between the logarithm of charge and the logarithm of resistivity for nylon treated with antistatic agents.

Though the curves are determined by very few points, several observations may be made.

Figures 13 and 14 are small portions of charge–reciprocal concentration plots. At the higher humidity many of the curves are not straight lines, indicating that the region covered is primarily in the toe of the curve. When the humidity is lowered, the charges generated are higher, and most of the plots are on the straight line portion of the curve. For most compounds the slope and intercept of the straight line portion of the curve appear to change with humidity.

The slope of the logarithm of resistivity–logarithm of concentration curve (Figures 15 and 16) for a given compound remains constant when the humidity is changed. Only the intercept is affected by the change.

Thus Figures 13–16 demonstrate that the constants B, n, and D in Equations 2 and 3 are dependent on the relative humidity of the surroundings.

When the logarithms of charge are plotted against the logarithms of resistivity as in Figures 17 and 18, the slopes and intercepts are not much affected by humidity. Moreover, the curves for the variety of antistatic finishes occur close together and generally

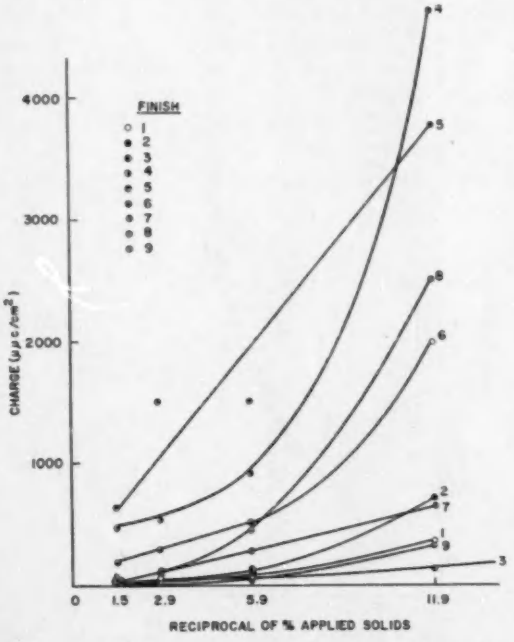


Fig. 13. Relation between charge and reciprocal concentration of various antistatic agents at high humidity.

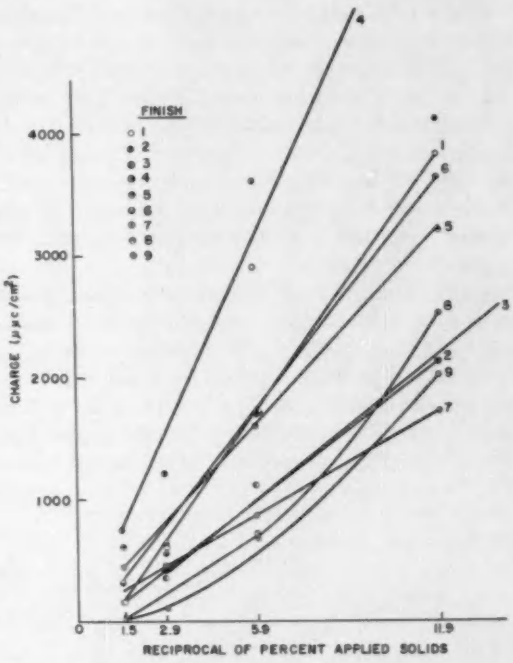


Fig. 14. Relation between charge and reciprocal concentration of various antistatic agents at low humidity.

within the confidence limits of Figure 12. The single exception, Finish 8, is one which has shown instability in other applications and consequently may have changed during the time required to complete the testing. Since the curves of all the antistatic agents are so close, it may be concluded that the nature of the finish is of little consequence in this type of graph. Thus the figures suggest that the static charge generated between an insulator and a metal under constant conditions of contact and separation is primarily a function of the surface resistivity of the insulator.

This finding has important practical implications, since it establishes the value of resistivity measurements in the study of antistatic agents. Previously, resistivity was regarded as just one of the factors which must be considered. Now standard electrical resistivity tests such as have been proposed [1] may be used with confidence to predict general performance with regard to static electrification. Furthermore, dielectric shielding [13] and other mechanisms suggested for the action of antistatic agents do not appear to be as significant in these cases as is a change in the conductivity.

If the slope and intercepts of curves relating the logarithm of charge with the logarithm of resistivity are independent of chemical type, then $-m$, the slope of such plots, also is independent of chemical structure. An inspection of Figures 10, 15, and 16 appears to confirm this. Thus in the range where the linear relation holds, antistatic agents may be characterized on a graph of logarithm of resistivity against logarithm of concentration by the intercept at a given concentration.

Götze, Brasseler, and Hilgers [11] treated viscose with a finish to achieve varying degrees of surface electrical conductivity. The voltage generated by these fabrics at three different velocities was determined. As a further test of Equation 5, the data reported by these workers were plotted as the logarithm of voltage versus the logarithm of specific resistance. Naturally, at constant capacity, voltage is proportional to charge. Figure 19 substantiates the straight line relation. Moreover, this figure demonstrates the fact that the slope of the curve is dependent on the speed of testing.

How can the slope of Equation 5, which depends on speed, be related to the slope of Equation 2, where resistivity is measured under conditions of constant level and flow of charge? This would be possible only if the slope of Equation 2 represents a limit. Since constant charge is approached as the speed of rubbing increases, it seems reasonable to assume that the limit is that of extremely high-speed rubbing.

The slope of the line relating logarithm charge and logarithm resistivity is determined by $(\log Q_2 - \log Q_1)/(\log R_2 - \log R_1)$ or $\log Q_2/Q_1$ per constant difference of resistivity. Examination of plots of the charge on tires and fabrics of different resistivity as a function of speed [4, 32] indicates that Q_2/Q_1 is a function of speed and tends to become constant at high speeds. Moreover, since the charges approach zero as the speed decreases, the ratio approaches 1. Since $\log 1 = 0$ and the slope in Equation 2 cannot be zero, the possibility of the slope representing the lower limit of velocity is

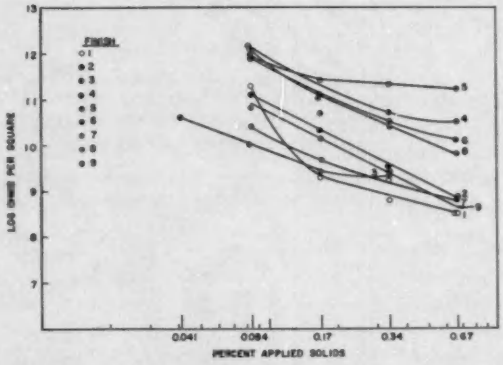


Fig. 15. Relation between the logarithm of resistivity and the logarithm of concentration of various antistatic agents at high humidity.

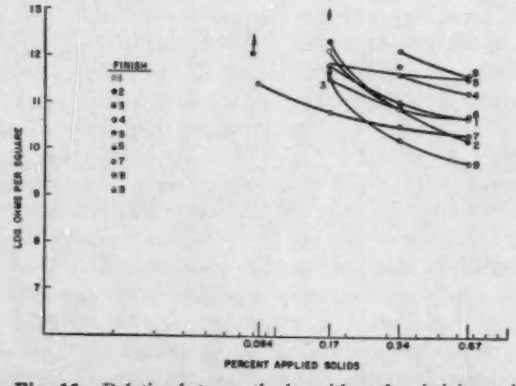


Fig. 16. Relation between the logarithm of resistivity and the logarithm of concentration of various antistatic agents at low humidity.

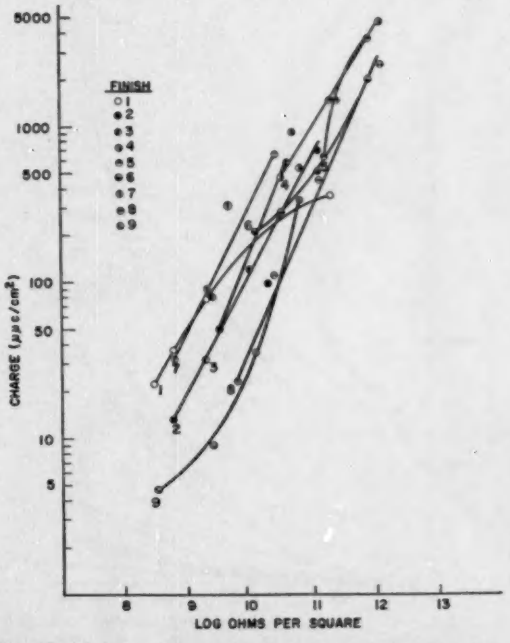


Fig. 17. Relation between the logarithm of charge and the logarithm of resistivity at high humidity.

eliminated. Evaluation of antistatic agents by resistivity methods then is equivalent to evaluation under conditions of high-speed rubbing, which, of course, are the most drastic circumstances.

Critical Resistivity Value

If, as Equation 5 indicates, surface resistivity is the critical factor in the generation of static charges, to what level should surface resistivity be brought in order to eliminate difficulties due to static electricity? Bulgin [5], Medley [32], and Ward [40] have calculated the critical resistances which would be required to control the formation of static electricity in specific situations.

Moreover, while no basis for the ratings is given, U.S. Patent 2,676,122 [27] contains data which permit construction of the following scale:

Log ohms/square	Antistatic rating
13.4+	Nil
12.4–13.4	Poor
11.8–12.4	Fair
11.1–11.8	Good
10.1–11.1	Very good
Less than 10.1	Excellent

To correlate measures of resistivity with practical experience, an attraction test was employed.

Treated fabric was rubbed vigorously by hand against a mounted piece of wool flannel. The sample then was passed slowly at a height of about 1 in. over a pile of cigarette ashes. The amount of ashes which the fabric picked up was described as "much," "some," "slight," or "none." Since the lightest ash particles are picked up to the greatest extent, it was necessary to use a fresh pile of ashes for each experiment.

For these experiments nylon taffeta, a plain weave Orlon, and a ribbed Dacron shirting material were treated with a binder and increasing concentrations of an antistatic agent. The purpose of the binder in this case was to minimize transfer of the antistatic agent. Table III shows the results of the attraction tests together with the surface resistivities of these fabrics.

The exact value of the critical resistivity appears to depend on the fabric. In general, however, samples with a log resistivity of less than 11 ohms per square are not likely to be troubled with static electricity. Between 11 and some point below 13.8, intermediate amounts of protection from static electricity exists. Since it has been shown that the charge of static electricity is dependent primarily on the surface resistivity of the fabric, it would appear that difficulties with static electricity are not likely to be encountered under circumstances where the logarithm of surface resistivity is less than 11 ohms per square. These values are in general agreement with the scale given above.

TABLE III

Fabric	Resistance, log ohms/square	Cigarette ash
Nylon	13.8+	Much
Nylon	12.3	Slight
Nylon	11.7	None
Nylon	10.5	None
Nylon	9.4	None
Orlon	13.8+	Much
Orlon	11.7	Slight
Orlon	10.4	Slight
Orlon	9.1	None
Orlon	8.6	None
Dacron	13.8+	Much
Dacron	12.1	Slight
Dacron	11.0	None
Dacron	10.0	None
Dacron	9.2	None

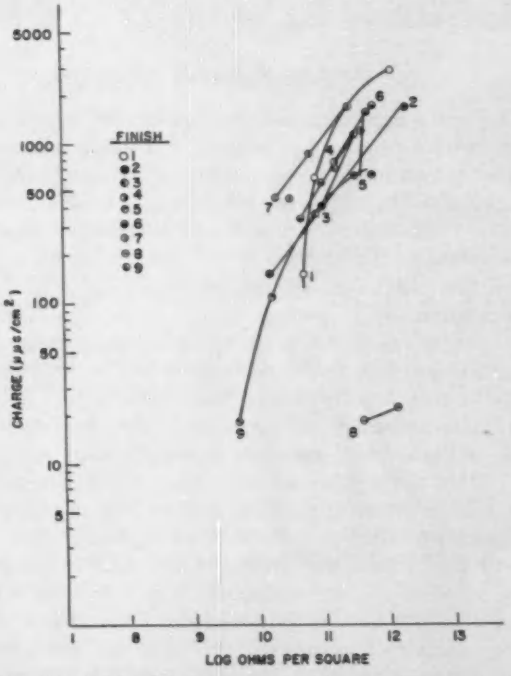


Fig. 18. Relation between the logarithm of charge and the logarithm of resistivity at low humidity.

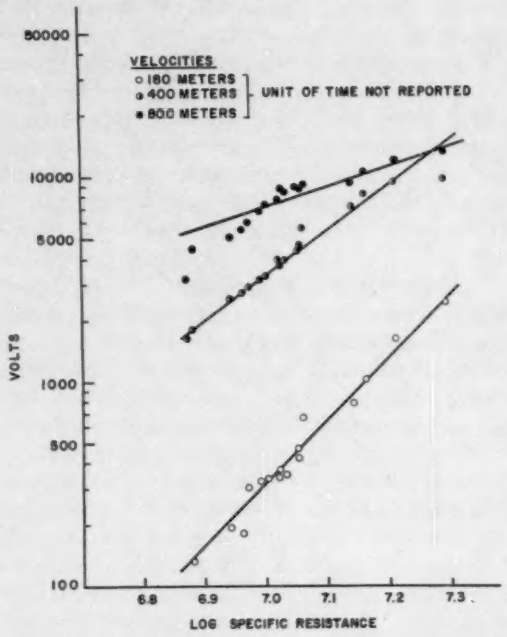


Fig. 19. Relation between the logarithm of voltage and the logarithm of specific resistance at different rubbing speeds. (Data from Götze et al. [11].)

Conclusions

For the concentrations investigated, the logarithm of surface resistivity of a fabric is a linear function of the logarithm of the quantity of antistatic agent applied. The slopes of such curves are fairly constant; thus the finish on a given fabric may be characterized by the intercept of the straight line portion of the curve or by the resistivity at a fixed concentration.

The charge on these fabrics developed by rubbing under constant conditions is inversely proportional to the concentration of applied antistatic agent. This relation is limited and shows deviations characteristic of the finish at extremes of concentration.

When test results on a fabric treated with different antistatic agents are plotted as logarithm of charge versus logarithm of resistivity, no significant difference due to chemical identity of the finish is apparent. While the intercept of such a plot contains two terms which are humidity-sensitive, the relation is independent of humidity. The slope and intercept of this curve appear to be affected only by the rate at which testing is performed. From these observations it is concluded that the action of the antistatic agents examined is dependent primarily on the surface resistivity change which they produce.

On the fabrics tested it was found that the material should be free of difficulties due to static electricity under those conditions where the surface resistivity has a logarithm of resistance of 11.0 or less ohms per square.

Acknowledgments

The author is indebted to Mr. N. A. Matlin for many fruitful discussions on this problem. The author also wishes to acknowledge the assistance of Mrs. Marie C. Harkins and Mr. Robert G. Petrella in carrying out the experimental work reported.

Literature Cited

1. American Association of Textile Chemists and Colorists, *Technical Manual and Yearbook* **31**, (1955), p. 140, Tentative Test Method 76-54.
2. Baker, C. A., *America's Textile Reptr.* 33 (July 16, 1953).
3. Ballou, J. W., TEXTILE RESEARCH JOURNAL **24**, 146 (1954).
4. Bulgin, D., *Brit. J. Appl. Phys.* Supp. No. 2, 83 (1953).
5. Bulgin, D., *ibid.*, 87 (1953).
6. Cadwell, S. M., Handel, N. E., and Benson, G. L., *Ind. Eng. Chem., News Ed.* **19**, 1139 (1941).
7. Cohn, E. M. and Guest, P. G., *Influence of Humidity upon the Resistivity of Solid Dielectrics and upon the Dissipation of Static Electricity*, U. S. Dept. of Int., Bur. of Mines Info. Circ. 7236 (1944).
8. Crugnola, A. M. and Thomas, G. R., *Instrumental Methods for Investigating Static Electricity on Fabric*, Quartermaster Research & Development Center, Textile Dying Laboratory Report No. 131 (July 1956).
9. Gill, E. W. B. and Alfrey, G. F., *Nature* **163**, 172 (1949).
10. Gonsalves, V. E. and van Dongeren, B. J., TEXTILE RESEARCH JOURNAL **24**, 1 (1954).
11. Götze, K., Brasseler, W., and Hilgers, F., *Melliand Textilber* **34**, 141 ff (1953).
12. Götze, K., Brasseler, W., and Hilgers, F., *ibid.*, 1142 (1953).
13. Graham, G. W., Third Canadian Textile Seminar (September 1952).
14. Grüner, H., *Faserforsch. und Textiltech.* **4**, 249 (1953).
15. Havenhill, R. S., O'Brien, H. C., and Rankin, J. J., *J. Appl. Phys.* **15**, 731 (1944).
16. Havenhill, R. S., O'Brien, H. C., and Rankin, J. J., *ibid.*, **17**, 338 (1946).
17. Hayek, M. and Chromey, F. C., *Am. Dyestuff Reptr.* **40**, 164 (1951).

18. Hayek, M. and Chromey, F. C., *ibid.*, 225 (1951).
19. Henry, P. S. H., *Brit. J. Appl. Phys.* Supp. No. 2, 31 (1953).
20. Hersh, S. P. and Montgomery, D. J., TEXTILE RESEARCH JOURNAL **22**, 805 (1952).
21. Hersh, S. P. and Montgomery, D. J., *ibid.*, **25**, 279 (1955).
22. Keggin, J. F., Morris, G., and Yuill, A. M., *J. Textile Inst.* **40**, 702 (1949).
23. Kirkwood, C. E., Bellamy, O. H., Kendrick, N. S., and Brown, H. M., TEXTILE RESEARCH JOURNAL **24**, 853 (1954).
24. Lehmicke, D. J., *Am. Dyestuff Reptr.* **38**, 853 (1949).
25. Levy, J. B. and Dillon, J. H., TEXTILE RESEARCH JOURNAL **26**, 953 (1956).
26. Liska, J. W. and Hansom, E. E., *Rubber Chem. & Tech.* **15**, 678 (1942).
27. McCarthy, J. R., U. S. Patent 2,676,122 (April 20, 1954).
28. McLean, H. T., *Am. Dyestuff Reptr.* **44**, 485 (1955).
29. Medley, J. A., *Nature* **166**, 524 (1950).
30. Medley, J. A., *Brit. J. Appl. Phys.*, Supp. No. 2, 23 (1953).
31. Medley, J. A., *ibid.*, 28 (1953).
32. Medley, J. A., *J. Textile Inst.* **45**, 123 (1954).
33. Morris, G. and Young, A. N. D., *Nature* **171**, 220 (1953).
34. Ott, R. V., U. S. Patent 2,421,430 (June 3, 1947).
35. Richards, H. F., *Phys. Rev.* **22**, 122 (1923).
36. Silsbee, F. B., *Static Electricity*, U. S. Dept. of Comm., Nat. Bur. of Stds. Circ. C438 (1942).
37. Sprenkmann, W., *Melliand Textilber.* **34**, 971 (1953).
38. Sweeney, J. W., *Evaluation of Antistatic Agents on Nylon Parachute Cloth*, Wright Air Development Center Tech. Report 54-513 (September 1955).
39. Teixeira, N. A. and Edelstein, S. M., *Am. Dyestuff Reptr.* **43**, 195 (1954).
40. Ward, G. R., *Am. Dyestuff Reptr.* **44**, 220 (1955).

Manuscript received March 13, 1958.

Structural Compactness of Woven Wool Fabrics and Their Behavior in Modern Washing Machines

Herman Bogaty, George H. Lourigan[1], and Hazel E. Harris

Harris Research Laboratories, Inc., Washington, D. C.

Abstract

A wide array of commercial all-wool fabrics have been subjected to physical analysis and to ten consecutive mild launderings in a modern automatic home washing machine. Many of the fabrics are shown to exhibit low levels of shrinkage in this test. The shrinkage of the fabrics of the same weave type is shown to be related to the cover factor of the cloth. A measure of compactness of fabric structure can be computed from the ratio of observed cover factor to the theoretically maximum weavable cover factor. This compactness ratio shows a good functional relationship to shrinkage in laundering for virtually all of the fabrics, irrespective of weave. This relationship indicates that a commercially acceptable fabric may be designed with respect to its compactness to give low levels of feltability in many repeated launderings.

Introduction

Many aspects of the felting of wool and of treatments for the production of washable wool received special attention during World War II and the period immediately thereafter. The impetus for the concentration during this period lay in the vast increase in wool utilization for military garments and the desire for conservation of this strategic material. As would be natural, evaluations of products and processes were conducted with the stringent military requirements in mind, and severe field laundering or equivalent procedures were often employed. The domestic washing machines of the time, being designed principally for the laundering of heavily soiled

[1] Union Carbide Chemicals Company.

cottons, offered little opportunity for milder washing. Thus, even where civilian utilization was considered, it was thought necessary for antifelting treatments to be capable of meeting severe washing procedures in the home as well.

While much effort was devoted to chemical and additive (e.g., resin and latex) treatments to achieve the desired antifelting effect, some investigations were undertaken in these laboratories [2, 3] and by Dutton [5, 6] on the role of fabric construction on felting during laundering in the absence of shrink-proofing treatments. The results of these studies indicated that substantial improvement in washability can result from changes in the construction of a knitted or woven fabric, and feltability is inversely related to some aspect of the compactness of the fabric structure. Nonetheless, under severe laundering conditions of evaluation, it was found necessary to conclude that "application of a shrink-resistant treatment to wool produces a greater effect in reducing laundering shrinkage than any modification of construction . . ." [3].

In more recent years, the situation with respect to the severity of laundering in domestic washing machines has changed substantially [1]. The development of automatic devices which permit control over a number of the various steps in the laundering process allows a mild washing procedure to be selected and to be performed without undue attention on the part of the housewife. Typical wool fabrics have been shown to be no more feltable in ten mild cycles in a modern washer than in two cycles employing more vigorous procedures [1].

Thus, a change in emphasis from military to civilian utilization and the potentiality of the modern automatic home washer for mild and simple laundering procedures as those prescribed for some synthetic or "easy-care" fabrics present new opportunities for the machine washing of wool materials in the home. The Wool Bureau and the International Wool Secretariat therefore suggested that a reinvestigation of the relationship between fabric construction and laundering shrinkage in the modern washer would be most timely, and they are sponsoring such a study in these laboratories. This study is part of a broader program designed to determine whether or not wool fabrics can be engineered to provide adequate washability in the home with no antifelting treatment or with much milder treatments than heretofore employed.

Materials and Methods

The general experimental approach was to examine commercial fabrics (as opposed to specially designed or handwoven materials used in some previous work) in a realistic washing situation.

A group of approximately 75 fabrics was obtained from commercial sources for use in this study; these represent fabrics which are being produced and sold by the textile industry today. For simplification in subsequent analysis, a smaller group was selected from this initial large group of fabrics for this study through the elimination of fabrics with very complex weaves, fabrics with diverse types and sizes of yarn used in the same warp or filling, knitted fabrics, and those materials which were not entirely composed of untreated wool. The residual group of 36 fabrics represents a diverse array of commercial woolen and worsted fabrics covering a wide range of weights (6.5–24 oz.), weaves (plain to five-harness), thread counts (16–127 threads/in.), yarn types, and end uses.

Samples were relaxed prior to test by immersion in a 0.1% nonionic wetting agent for at least 1 hr. and air dried on a flat surface without tension. Laundering was conducted in a typical 1957 model automatic home washing machine (Maytag Model 140) employing a mild washing procedure described in detail elsewhere [1]. In brief, each laundering cycle comprises a 3-min. suds period with a commercial light duty anionic detergent and two rinse steps with intermediate and final centrifugation for a total washing time of 20 min. Controls on the machine are preset to give "normal" (high) water level, warm (100° F.) water, and "modern fabrics" agitation and spinning speed (one-third slower than the "regular fabrics" setting).

Physical analysis of the fabrics comprised determination of the weave and, after conditioning in a standard atmosphere (70° F., 65% relative humidity), determination of thread count and yarn size. The latter was determined from the length straightened just enough to remove crimp and the weight of a 3-yd. sample of yarn removed from the fabric.

The observed warp and filling cover factors were calculated from the equation

$$K_0 = 1.073 \frac{n}{\sqrt{N}}$$

in which n is the thread count, N is the cotton yarn number, and 1.073 is the ratio between the square root of the densities of cotton and wool.

TABLE I. Physical Properties of 36 Commercial Fabrics

Fabric code number	Weave	Threads/in.		Yarn size, cotton count, singles equiv.		Oz./sq. yd.	Percent felting shrinkage in 10 mild machine launderings			Compactness ratio
		Warp	Filling	Warp	Filling		Warp	Filling	Area	
55	Plain	53	50	10.6	10.0	7.3	0.6	0.2	0.8	.91
84	Plain	59	47	13.7	12.3	5.7	1.2	0.5	1.7	.81
82	2/1 Twill	73	53	13.6	13.8	7.0	2.6	0.5	3.0	.79
65	2/2 Twill	60	60	8.0	7.4	11.7	3.0	0.5	3.5	.93
4	Plain	61	53	16.3	15.2	5.2	3.0	1.0	4.0	.81
83	3/2 Twill	98	61	15.9	15.3	7.6	4.2	1.4	5.6	.79
57	Plain	56	44	11.7	10.3	6.9	4.5	1.3	5.7	.83
86	2/1 Twill	60	39	13.1	14.1	6.4	4.9	1.1	5.9	.78
62	3/2 Twill	43	47	5.4	5.2	12.5	5.4	0.9	6.3	.79
47	2/2 Twill	69	61	15.0	13.8	7.1	5.0	2.2	7.1	.74
28	2/2 Twill	54	34	5.1	5.2	13.7	7.4	1.1	8.3	.81
56	2/2 Twill	123	73	18.3	18.8	8.1	6.6	2.0	8.4	.94
19	Plain	55	45	13.9	13.9	4.9	5.8	2.8	8.4	.75
29	2/2 Twill	52	40	6.2	6.6	11.5	6.1	4.0	9.6	.78
77	2/1 Twill	44	48	9.4	9.6	8.3	7.5	2.2	9.6	.72
59	3/2 Twill	127	96	21.9	26.6	7.3	5.2	4.8	9.8	.92
81	2/2 Twill	44	48	9.2	8.8	8.4	8.0	2.4	10	.66
79	Plain	36	34	9.4	8.7	5.5	6.6	4.1	10	.66
92	Plain	32	32	7.1	6.3	6.9	7.0	4.0	11	.70
78	Plain	39	35	8.8	9.1	6.4	7.8	3.7	11	.70
2	2/2 Twill	65	75	17.0	18.9	5.9	7.1	4.8	12	.73
73	Plain	40	43	9.6	11.5	7.8	7.6	4.6	12	.76
61	2/2 Twill	38	34	5.5	5.1	11.3	8.8	4.4	13	.67
87	2/2 Twill	31	30	4.8	2.3	16.1	6.4	6.9	13	.68
80	Plain	32	28	6.6	6.7	6.9	8.3	5.1	13	.66
89	2/1 Twill	35	36	6.9	6.7	8.2	9.6	4.7	14	.66
74	Plain	40	36	10.6	10.2	5.9	9.8	4.4	14	.67
93	2/2 Twill	25	32	4.1	2.8	13.1	9.7	9.0	18	.64
88	3/1 Twill	32	25	4.7	3.2	11.1	13	8.4	20	.60
8	2/2 Twill	39	34	6.8	6.7	8.4	11	9.9	20	.61
16	2/1 Twill	32	27	6.5	6.6	6.7	14	12	24	.55
30	2/2 Twill	55	44	14.3	8.1	6.9	19	6.4	24	.62
63	2/1 Twill	35	27	6.1	5.9	7.6	19	7.4	25	.59
90	3/1 Twill	26	16	5.5	2.0	9.3	19	13	29	.45
49	Plain	34	37	9.0	8.9	6.1	21	14	32	.68
53	Fancy 5-harness weave	30	24	6.0	5.6	6.9	24	33	48	.45

Shrinkage

The felting shrinkage in laundering of the fabrics was determined from the distance between marks on the fabrics after ten mild launderings. It was expressed as a percentage of the relaxed fabric dimension and is the mean of three readings in both the warp and filling directions. Two or more specimens were subjected to laundering tests in different runs. The shrinkage in area of the test specimens was calculated by subtracting one hundredth of the product of warp and filling shrinkage (in percent) from the sum of the percent warp and filling shrinkage.

Results of Tests

The data describing the physical analysis of the construction of the 36 test fabrics are given in Table I, in increasing order of the area felting shrinkage in ten mild launderings. The diversity in fabric structure is to be noted, and the wide range in laundering shrinkage observed is not unexpected. What may be surprising, however, is the relatively low level of felting shrinkage observed in mild laundering for so many of the fabrics studied. In the parent group of 75 commercial fabrics, over one third exhibited shrinkages in area of less than 10% after ten launderings [1].

Examination of the construction data in Table I does not immediately suggest any obvious relationship between construction and felting, except for the trend to lower thread counts in the more feltable samples. Nor does there seem to be any relationship between felting and fabric weight. When the cover

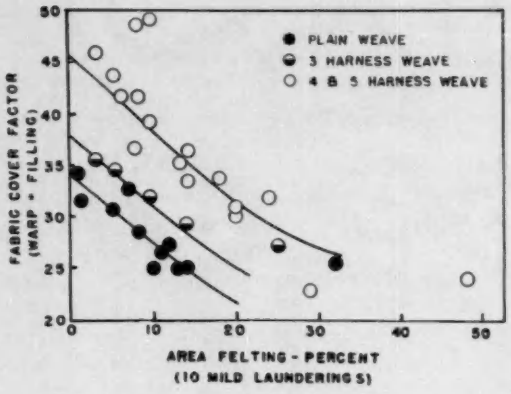

PLAIN WEAVE
3 HARNESS WEAVE
4 & 5 HARNESS WEAVE
FABRIC COVER FACTOR (WARP + FILLING)
AREA FELTING - PERCENT (10 MILD LAUNDERINGS)

Fig. 1

factors are computed, however, the relationship between this measure of fabric compactness and laundering shrinkage, as shown in Figure 1, becomes clearer. This functional relationship is similar to that observed in previous studies [2, 3]. The present work demonstrates that the principle appears to be quite general and operates in the case of a wide array of commercial fabrics. Moreover, the data suggest the possibility of designing a fabric in terms of its weave and cover factors, so that its feltability will be at any given level in terms of a modern washing procedure.

It was thought useful to attempt a more unified picture of the data of Figure 1 which would describe the compactness of a fabric without reference to weave. Recourse was made to the theoretical treatment of Love [7] and of Dickson [4], who have considered the maximum weavability of fabric structures of varying kinds. These workers have expanded the geometry of fabrics as described by Peirce [8] to include weaves from plain to five-harness satins, of fibers of various densities, and of yarns in warp and filling of different sizes in the same cloth.

Love has published an extremely useful set of graphs [7] which depict the cover factors of fabrics of maximum weavability for various weaves and for various ratios of yarn size. These cover factors are assumed to describe fabrics of maximum theoretical compactness that may be woven from a given set of yarns in a given weave. (Other conventions assumed in the geometrical derivation are that yarns are flexible but incompressible cylinders, that the bulk density of yarns in a fabric is a constant value, and that the conventional diameter of a yarn is inversely proportional to the density of the fiber of which it is made.) The closeness with which a real fabric approaches the theoretical maximum compactness may be computed in several ways. The method selected herein is to define a compactness ratio C as

$$C = \frac{\frac{K_{L,0}}{K_{L,T}} + \frac{K_{S,0}}{K_{S,T}}}{2}$$

in which $K_{L,0}$ is the largest observed cover factor, either warp or filling; $K_{S,0}$ the other or smaller observed cover factor; $K_{L,T}$ the maximum theoretical cover factor in one direction for the same weave and yarn size ratio as in the observed fabric; and $K_{S,T}$ the theoretically maximum cover factor in the other direction, given $K_{L,T}$. The values for the maximum theoretical cover factors which vary with weave and yarn size were taken from Love's graphs.

The compactness ratios for the fabrics studied are given in Table I, and plotted against shrinkage in ten launderings in Figure 2.

The value of C approaches 1.0 for maximum compactness and in commercial cloth is in the region of 0.4 for open, sleazy structures. Examination of Figure 2 indicates that a definite relationship exists between the compactness of a wool fabric and the extent to which it will resist felting in laundering. Indeed, the relationship shown is considered quite close in view of the many varied constructions included.

There are, of course, several examples of anomalous behavior; e.g., samples 56, 59, and 49 all exhibit greater levels of shrinkage than their compactness ratios would predict. These fabrics are being ex-

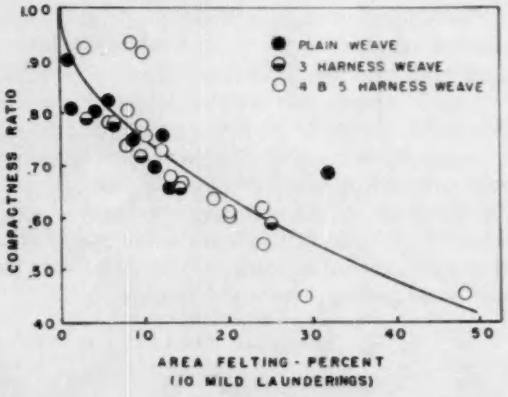


Fig. 2

amined in further detail to determine whether balance in the thread count, the relative fineness of the yarns and their bulk density, or other characteristics of the yarns or fibers can explain their behavior.

While the generality of the relationship between fabric compactness and feltability indicates that fabric structure is the principal controlling factor, other features of construction are being examined in a number of these fabrics. The contributions to felting of fiber characteristics—crimp, diameter, and staple length—and of yarn crimp and twist are being studied for a number of the fabrics. Also planned for future work is an attempt to design and manufacture fabrics of controlled compactness ratio, particularly of high values corresponding to low laundering shrinkage; this will verify the ability to "engineer" washable wool fabrics through construction alone.

Acknowledgment

The assistance of Mrs. Lois Blair and of Mrs. Octavia Vollmer in making many of the measurements reported is sincerely appreciated. The sponsorship of this research program by the International Wool Secretariat and the substantial assistance and discussion of the program by Dr. Gerald Laxer of The Wool Bureau, Inc. are gratefully acknowledged.

Literature Cited

1. Bogaty, H. and Harris, H. E., *Am. Dyestuff Reptr.* **47**, 369 (1958).
2. Bogaty, H., Weiner, L. I., Sookne, A. M., Cozart, M. L., and Harris, M., TEXTILE RESEARCH JOURNAL **21**, 895 (1951).
3. Bogaty, H., Weiner, L. I. Sookne, A. M., and Harris, M., TEXTILE RESEARCH JOURNAL **21**, 102 (1951).
4. Dickson, J. B., TEXTILE RESEARCH JOURNAL **24**, 1083 (1954).
5. Dutton, W. A., *J. Textile Inst.* **37**, P212 (1946).
6. Dutton, W. A., *J. Textile Inst.* **40**, P636 (1949).
7. Love, L., TEXTILE RESEARCH JOURNAL **24**, 1073 (1954).
8. Peirce, J. T., *J. Textile Inst.* **28**, T45 (1937).

Manuscript received March 24, 1958.

Cyanoethylation of Cotton in Aqueous Medium

Norbert M. Bikales and Lorence Rapoport

Stamford Laboratories, Research Division, American Cyanamid Company, Stamford, Connecticut

Abstract

An investigation was made of the cyanoethylation of cotton using small quantities of acrylonitrile dissolved or dispersed in aqueous sodium hydroxide solution. As compared with conventional processes, the rate of reaction and the maximum degree of cyanoethylation were both found to be lower. The losses of acrylonitrile in side reactions were relatively small and approached the minimum obtainable in the best processes previously reported. A study of the physical properties of the product showed the importance of reaction conditions in determining the properties of cyanoethylated cotton.

Introduction

As a result of Compton's finding [3] of the improved properties of partially cyanoethylated cotton, notably complete rotproofness, a considerable effort has been made to develop practical procedures for the treatment. Compton's original two-step process has been modified by systematic investigation of the variables [2, 4, 6, 12, 19], by dilution of acrylonitrile with an organic solvent [2, 6], by the use of swelling salts to accelerate selectively the cellulose-acrylonitrile reaction [1], and by elimination of the alkali pretreatment step of the process [5, 10]. Other variations included reaction in the vapor phase [4, 5] or in a molten metal bath [4, 11]. The primary aim of these improved processes was to reduce the amount

of acrylonitrile lost in the side reaction with water to form β, β'-oxydipropionitrile. In the original two-step process, these losses amounted to at least five times as much as the quantity of acrylonitrile actually combining with the cellulose. The later processes brought this amount to about equal weights being lost and reacting, or even less in some cases.

The authors now wish to report further work carried out with the aim of improving the cyanoethylation process. The present approach, in contrast to the earlier procedures, utilizes only small quantities of acrylonitrile dissolved (or dispersed) in aqueous sodium hydroxide solutions. It was hoped that this process would not only reduce losses, but also eliminate the recovery of unreacted acrylonitrile which is necessary in conventional processes. A somewhat similar procedure had been used in the classical studies of MacGregor with solutions of cellulose xanthate [13, 14] and by Miller and Flowers in the cyanoethylation of lignocellulose [16]. After the completion of this investigation, a report appeared describing the reaction of acrylonitrile with cellulose in aqueous medium to give carboxyethylcellulose [20].

Procedure

A typical procedure of cyanoethylation in aqueous medium was as follows.

A 10-g. skein of 40/2 greige yarn (Standard-Coosa-Thatcher Co.) was added to a stoppered 500-ml. flask equipped with mechanical stirrer and containing 200 g. of a 10% aqueous sodium hydroxide solution. The temperature was maintained at 15–20° C. After the cotton was thoroughly impregnated with the alkaline solution, 6.4 g. of acrylonitrile (AN) was added, and reaction was allowed to proceed for 4 hr. The mixture was then neutralized, and the cotton was washed, dried, and analyzed for nitrogen content. Since there was virtually no remaining acrylonitrile, the efficiency of the reaction could be determined directly from the percent nitrogen and the weight of the cotton. The efficiency was expressed by an AN ratio defined as follows:

$$\text{AN ratio} = \frac{\text{weight of AN not reacted with cotton}}{\text{weight of AN reacted with cotton}}$$

The numerator corresponds to the difference between the quantity of acrylonitrile initially added and the denominator of the ratio. A low AN ratio, therefore, is indicative of an efficient reaction.

In the experiment described above, the average nitrogen content of the cotton was found to be 3.6%, and the AN ratio was 3.5. Under the same conditions, but using lignocellulose, Miller and Flowers obtained 2.5% N [16]; the AN ratio, when calculated as above, was 5.1.

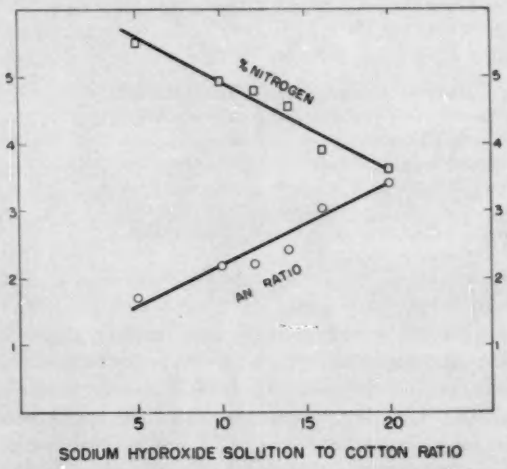


Fig. 1. Effect of the sodium hydroxide : cotton ratio on the percent nitrogen and the AN ratio (10 g. of cotton; 10% NaOH; 6.4 g. of AN; 4 hr. at 15–20° C.).

Effect of Variables on the Reaction

A systematic study of variables was undertaken with the hope of finding conditions giving the desired degree of cyanoethylation (3–4% N) with minimum losses of acrylonitrile in side reactions. A practical difficulty in this system was that usually several variables were affected per single change in the proportions of reactants.

Ratio of Sodium Hydroxide Solution to Cotton

Experiments were carried out under the same conditions as described above but with varying weights of sodium hydroxide solution (50–200 g.). The results, shown in Figure 1, indicate the degree of cyanoethylation to be inversely proportional and the AN ratio to be directly proportional to the sodium hydroxide solution : cotton ratio. At a ratio of 5, the caustic solution was completely soaked up by the cotton, but the efficiency of the reaction was nevertheless better than with the larger volumes of solution. The AN ratios found here are considerably more favorable than those obtained with the use of the standard two-step procedure [4].

Figure 1 can also be considered as a plot of the degree of cyanoethylation as a function of the acrylonitrile concentration, at a constant acrylonitrile : cotton ratio. The ratio of sodium hydroxide to cotton was, of course, also affected in these experiments.

Amount of Acrylonitrile

The general procedure was repeated, but at a constant sodium hydroxide solution : cotton ratio of 10, and with varying amounts of acrylonitrile. Figure 2 shows a linear relationship between the degree of cyanoethylation and the amount of acrylonitrile added. The AN ratio was calculated to be virtually constant in these runs, varying from 1.9 to 2.2. Similar results were obtained with 12% sodium hydroxide, but the percent nitrogen obtained was higher at comparable acrylonitrile levels (Figure 2) and the AN ratio was therefore lower (1.5–1.8). A reaction time of only 2 hr. was used in order to minimize hydrolysis [6].

Figure 2 is a plot of the percent nitrogen as a function not only of the acrylonitrile concentration but also of the acrylonitrile : cotton ratio. The latter variable was studied by the experiments shown in Table I. In these runs, the acrylonitrile concentration was kept constant, but the acrylonitrile : cotton ratio was changed which, of course, also affected the solution : cotton ratio. The highest nitrogen content was obtained at the highest acrylonitrile : cotton ratio, in spite of the fact that the simultaneous change in the sodium hydroxide solution : cotton ratio must have tended to counteract this effect (Figure 1). Thus, both the acrylonitrile concentration and the acrylonitrile : cotton ratio are important variables.

Sodium Hydroxide Concentration

A series of runs was made at 15–20° C., with a sodium hydroxide solution : cotton ratio of 10 and 3.2 g. of acrylonitrile per 100 g. of alkaline solution. The concentrations of sodium hydroxide were varied from 5.7 to 20% (Figure 3). The time of reaction was 4 hr. for runs with concentrations of up to 10% and 2 hr. with the more concentrated solutions.

It is apparent that increasing the sodium hydroxide concentration up to about 13% resulted in higher degrees of cyanoethylation. The nitrogen content decreased, however, when the alkali concentration exceeded this value. In these experiments, the ratio of sodium hydroxide to cellulose, which is probably also a significant variable [9, 19], changed with concentration.

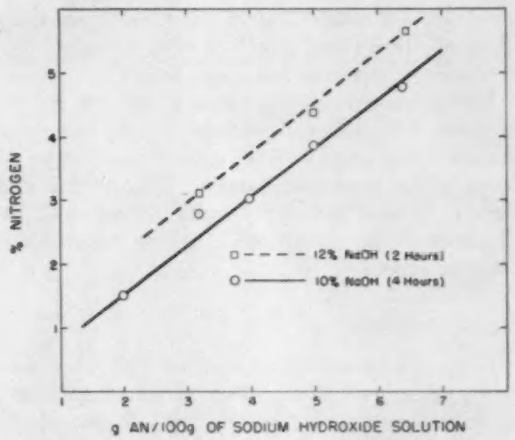


Fig. 2. Effect of the amount of acrylonitrile used on the percent nitrogen (10 g. of cotton; 100 g. of NaOH solution; 15–20° C.).

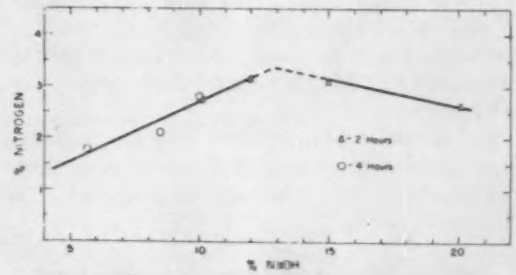


Fig. 3. Effect of the sodium hydroxide concentration on the percent nitrogen (10 g. of cotton; 100 g. of NaOH solution; 3.2 g. of AN; 15–20° C.).

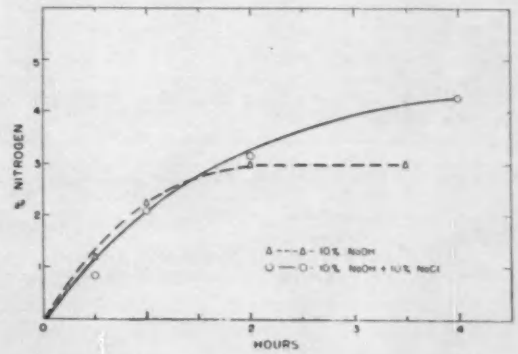


Fig. 4. Effect of sodium chloride on the rate of cyanoethylation (10 g. of cotton; 10 g. of NaOH, 10 g. of NaCl, and 80 g. of water; 4.0 g. of AN; 15–20° C.).

An experiment was made combining the optimum sodium hydroxide solution : cotton ratio, 5, with the optimum alkali concentration, or 12%. After 2 hr. at 15–20° C., using 3.2 g. of acrylonitrile per 10 g. of cotton, the product contained 3.6% nitrogen. The AN ratio in this experiment was only 1.1.

The maximum cyanoethylation found with the use of about 13% sodium hydroxide can be correlated with the maximum swelling of cellulose known to occur at the same concentration [15]. Grant and co-workers have observed a similar maximum at approximately this concentration in the conventional two-step procedure [9].

Use of Additives

It has previously been reported that salts with ability to swell cellulose, such as sodium thiocyanate, increase the rate of cyanoethylation in procedures where a relatively large excess of acrylonitrile is used [1].

In aqueous medium, however, an increase in the degree of cyanoethylation was noted with these salts in only a few cases. Furthermore, the combined swelling action of the alkali and the salt rendered the cotton slick and gelatinous, making this approach unsatisfactory.

In contrast, sodium chloride, which is ineffective in procedures using a large excess of acrylonitrile [1], proved valuable in the aqueous procedure. This is illustrated in Figure 4. The conditions studied were: 10 g. of cotton, 4.0 g. of acrylonitrile; 15–20° C.; composition of aqueous solution: 10 g. of sodium hydroxide, 10 g. of sodium chloride, and 80 g. of water. A control was also run, in which the salt was replaced by 10 g. of water. Figure 4 shows that the salt had no significant effect on the rate of reaction (up to 2 hr.), but that with it reaction continued for a longer time. The maximum nitrogen content obtained with the salt was 4.2% vs. 3.0% for the control; the AN ratios were 1.1 and 2.1, respectively. The effect of sodium chloride concentration is seen in Table II. A concentration of about 10% appears to be optimum.

Thus, sodium chloride only extends the length of time during which acrylonitrile is available for reaction. This suggests that it "protects" the acrylonitrile from side reactions, possibly by salting it out from solution, while the relatively slow cyanoethylation of cotton proceeds. The ineffectiveness of swelling salts in this procedure is not surprising, since swelling would not be expected to be significantly increased by them beyond the state achieved by the high alkali concentrations used.

TABLE I. Effect of the Acrylonitrile : Cotton Ratio *

Cotton, g.	AN : cotton ratio	Sodium hydroxide solution : cotton ratio	% Nitrogen
3.2	1.0	31	4.7
5.0	0.64	20	3.5
10.0	0.32	10	2.8

* Conditions: 3.2 g. of acrylonitrile, 100 g. of 10% sodium hydroxide solution; 4 hr. at 15–20° C.

TABLE II. Effect of Sodium Chloride Concentration *

Water, g.	Sodium chloride, g.	% Nitrogen	AN ratio
90	—	3.0	2.1
85	5	3.6	1.5
80	10	4.2	1.1
75	15	4.3	1.0

* Conditions: 10 g. of cotton; 4.0 g. of acrylonitrile; 10 g. of sodium hydroxide; 4 hr. at 15–20° C.

Time of Reaction

The effect of time under typical conditions is seen in Figure 4. Without salt, the reaction was essentially complete in 2 hr. In some runs, however, a slight increase in nitrogen content (0.2%) was observed after an additional 2 hr., at which time all acrylonitrile had disappeared.

Since attempts to shorten reaction times with additives were unsuccessful, the only practical way found to increase the rate of reaction was by the use of a larger excess of acrylonitrile. This is shown in Table III. In these runs, 3–4% nitrogen was reached in about 1 hr. Analysis showed that a substantial quantity of acrylonitrile remained in the reaction mixture, however.

Temperature of Reaction

The effect of temperature on the extent of reaction was investigated (Table IV). It was found that lower degrees of cyanoethylation resulted when temperatures either lower or higher than 15–20° C. were used. At 35° C., with a sodium hydroxide solution : cotton ratio of 10 and an acrylonitrile : cotton ratio of 0.32, it was not possible to exceed 1.1% nitrogen when the alkali concentration was varied

TABLE III. Use of Excess Acrylonitrile *

Acrylonitrile, g.	Time, min.	% Nitrogen
6.4	60	3.2
6.4	110	4.1
8.0	60	4.0

* Conditions: 10 g. of cotton; 100 g. of 10% sodium hydroxide solution; 15–20° C.; acrylonitrile was not completely soluble in reaction mixture.

from 2 to 12%. These experiments indicate that the temperature range initially chosen (15–20° C.) on the basis of prior work [16] was the optimum for cyanoethylation in aqueous medium, and that the elimination reaction (cleavage of cyanoethyl groups) is strongly temperature-dependent [6, 13, 14].

Physical Properties

It became apparent very early in this work that the physical properties of cotton cyanoethylated in aqueous medium were significantly different from those of cotton treated by the conventional methods. In general, the cotton of this process appeared to be more highly swollen and to have less luster; in some cases, it became gelatinous on contact with water and harsh when completely dry. The tensile strength was lower than that of ordinary cyanoethylated cotton, but the elongation was significantly higher (Table V). A determination of moisture regain showed a value of 6.7% as compared with 5.4% for ordinary cyanoethylated cotton and 7.8% for the untreated control. The heat resistance was of the same order as that of cotton treated by the two-step procedure to an equivalent nitrogen content. A product with some similar properties was recently obtained by mercerization of cotton in the slack condition [8]. The appearance and tensile strength improved when the ratio of sodium hydroxide solution to cotton was decreased (Table V). It was also observed in a qualitative way that the appearance and hand were improved by the use of higher temperatures or lower alkali concentrations, i.e., by conditions which minimized swelling.

The most striking difference, however, was in the resistance of the cotton to microbiological degradation. Whereas cotton cyanoethylated by the conventional processes suffers no loss in tensile strength upon prolonged soil burial, provided that it contains at least 3% nitrogen [3], cotton cyanoethylated in aqueous medium lost most of its strength or disintegrated completely within two weeks, even though it was cyanoethylated to as much as 5.5% nitrogen. Carrying out the reaction under an atmosphere of nitrogen to prevent oxycellulose formation did not improve the properties of the cotton.

TABLE IV. Effect of Temperature on the Degree of Cyanoethylation *

Water, g.	Sodium hydroxide, g.	Time, hr.	Temperature, ° C.	Nitrogen, %
88	12	2	15–20	3.1
88	12	2	35	0.6
90	10	2	8–10	1.9
90	10	2	15–20	2.7
90	10	4	room	1.4
90	10	2	35	0.7
91.5	8.5	4	15–20	2.1
91.5	8.5	2	room	1.4
91.5	8.5	2	35	0.8
94.5	5.5	2	35	0.9
94.5	5.5	1	35	1.1
98	2.0	2	35	0.7

* Conditions: 10 g. of cotton; 3.2 g. of acrylonitrile.

TABLE V. Physical Properties of Cotton Cyanoethylated in Aqueous Medium *

Sample	Sodium hydroxide solution : cotton ratio	Tensile strength, g.	Elongation, %
Untreated	—	585	4.2
Cyanoethylated, two-step	—	795	5.5
A†	20	425	9.5
B†	14	610	8.0
C†	12	655	11.5
D†	10	720	11.0

* Measurements made at 21° C. and 65% RH; 40/2 yarn.
† Reaction carried out for 4 hr. at 15–20° C. with 10% NaOH and acrylonitrile : cotton ratio of 1 : 3.

In an effort to account for these differences in microbiological resistance, X-ray diffraction patterns were obtained. A considerable degree of deorientation was noted in samples which had been cyanoethylated in aqueous medium, whereas no significant change from untreated cotton was observed in products cyanoethylated by conventional methods, thus providing a correlation with rot resistance. This is shown in Figures 5 and 6. Deorientation and decrystallization are known to affect adversely the microbiological resistance of cellulose [17, 18].

An indication that deorientation or similar effects caused solely by the strong alkali were not the only factors to be considered was obtained by subjecting cotton to the action of 10% sodium hydroxide for 4 hr. at 15–20° C. After neutralization and washing, the cotton was immediately cyanoethylated by the two-step procedure to a nitrogen content of 4.2%. This sample lost no strength upon six weeks of soil burial, even though the X-ray diffraction pattern indicated a slight degree of deorientation (but much less than shown in Figure 6).

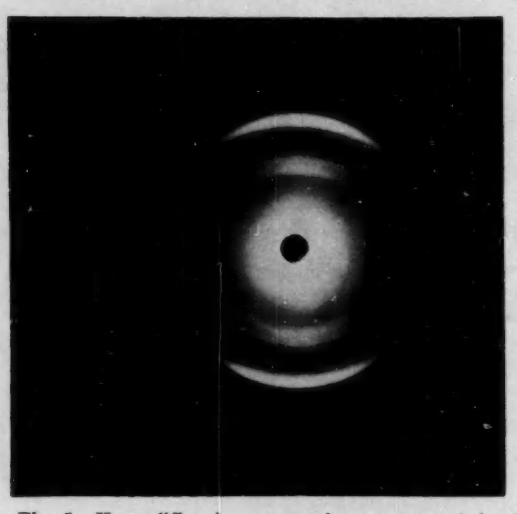


Fig. 5. X-ray diffraction pattern of cotton cyanoethylated by the two-step procedure; identical with that of native cellulose.

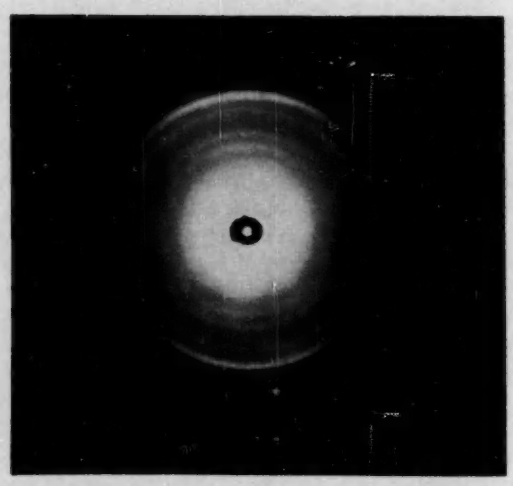


Fig. 6. X-ray diffraction pattern of cotton cyanoethylated in aqueous medium, showing deorientation of the cellulose.

The possibility that partial hydrolysis of cyanoethyl groups may have contributed to the lack of microbiological resistance was also investigated. Carboxyethyl determinations showed that cotton treated by the aqueous procedure generally had a somewhat higher acid content, about 0.03–0.05 meq./g., as compared with 0.02–0.03 meq./g. for cotton treated by the conventional two-step procedure. As it has been reported that the presence of relatively large amounts of carboxyethyl groups results in poor performance in the soil burial test because of intense swelling [19], it is probable that this factor also was important here. Further evidence for hydrolysis was the faint odor of ammonia noticeable during reaction. Hydrolysis of acrylonitrile could, of course, have contributed to this effect, but it was noted that at least in some instances a portion of the cotton actually dissolved in the alkali, indicating that cyanoethyl groups chemically combined with cellulose had been subjected to hydrolysis.

Differential dyeing of cotton cyanoethylated in aqueous medium to a nitrogen content of 3.8% gave a blue-purple color instead of the red usually found [7]. The uniformity appeared to be satisfactory. The use of a large excess of acrylonitrile (two parts per part of cotton) to overcome any possible nonuniformity gave a product which still had a blue color on differential dyeing and disintegrated in the soil burial test. X-ray examination showed a considerable degree of deorientation. It is likely, therefore, that the poor microbiological resistance is not primarily the result of nonuniformity of cyanoethylation, but that deorientation and hydrolysis may be important factors.

Conclusions

The cyanoethylation of cotton in aqueous medium proceeds at a substantially slower rate than in conventional processes, and the maximum degree of cyanoethylation obtainable falls far short of full cyanoethylation.

Under optimum conditions, i.e., at 15–20° C., using a sodium hydroxide solution : cotton ratio of 10 or less, an alkali concentration of 10–12%, and an additive such as sodium chloride, the amount of acrylonitrile lost in side reactions is roughly equal to the amount of acrylonitrile that reacts with the cotton. This is considerably better than in the con-

ventional two-step process; but equally satisfactory or better results have been obtained in other recently developed procedures [1, 2, 5, 10, 11].

The physical properties of cotton cyanoethylated in the slack condition by the procedure of this report reflect the drastic conditions of treatment to which the yarn was subjected. All samples were notably deficient in the most important characteristic of ordinary cyanoethylated cotton, namely microbiological resistance. Probable factors in this deficiency are deorientation of the cellulose and partial hydrolysis of cyanoethyl groups.

Acknowledgments

The authors wish to acknowledge the contributions of A. H. Gruber, Ann L. Hayford, G. Lamb, Dorothy H. Patt, L. R. Pritchard, and Bereit A. Wilcox.

Literature Cited

1. Bikales, N. M., Gruber, A. H., and Rapoport, L., *Ind. Eng. Chem.* **50**, 87 (1958).
2. Bikales, N. M. and Gruber, A. H., unpublished work.
3. Compton, J., Martin, W. H., Word, B. H., Jr., and Thompson, D. D., *Textile Ind.* **117**, 138A (1953).
4. Compton, J., Martin, W. H., Word, B. H., Jr., and Barber, R. P., TEXTILE RESEARCH JOURNAL **26**, 47 (1956).
5. "Cyanoethylation of Cotton," A Joint Report by Institute of Textile Technology, American Cyanamid Company, and Monsanto Chemical Company (Sept. 1956); also, *Am. Textile Reptr.* **71**, No. 1, 8 (1957).
6. Daul, G. C., Reinhardt, R. M., and Reid, J. D., TEXTILE RESEARCH JOURNAL **25**, 246 (1955).
7. Fordemwalt, F. and Kourtz, R. E., TEXTILE RESEARCH JOURNAL **25**, 84 (1955).
8. Goldthwait, C. F. and Murphy, A. L., TEXTILE RESEARCH JOURNAL **25**, 47 (1955).
9. Grant, J. N., Greathouse, L. H., Reid, J. D., and Weaver, J. W., TEXTILE RESEARCH JOURNAL **25**, 76 (1955).
10. Gruber, A. H. and Bikales, N. M., TEXTILE RESEARCH JOURNAL **26**, 67 (1956).
11. Janssen, H. J., DuPré, A. M., Haydel, C. H., Seal, J. F., and Vix, H. L. E., *Ind. Eng. Chem.* **50**, 76 (1958).
12. Klein, E., Weaver, J. W., Webre, B. G., and Jurgens, J. F., TEXTILE RESEARCH JOURNAL **27**, 50 (1957).
13. MacGregor, J. H. and Pugh, C., *Proc. XIth Intern. Congr. Pure & Appl. Chem.* (London) **5**, 123–31 (1947); Publ. 1953.
14. MacGregor, J. H., *J. Soc. Dyers Colourists* **67**, No. 2, 66 (1951).
15. Mark, H., "Physik und Chemie der Cellulose," Berlin, Julius Springer, 209–228 (1932).
16. Miller, H. F. and Flowers, R. G., U. S. Patent 2,535,690 (1950).
17. Perlin, A. S., Michaelis, M., and McFarlane, W. D., *Can. J. Research* **25C**, 246 (1957).
18. Siu, R. G. H., "Microbial Decomposition of Cellulose," New York, Reinhold Publishing, 256–259 (1951).
19. Weaver, J. W., Klein, E., Webre, B. G., and DuPré, E. F., TEXTILE RESEARCH JOURNAL **26**, 518 (1956).
20. Yashunskaya, A. G., Rogovin, Z. A., and Berlin, A. A., *Zhur. Priklad. Khim.* **29**, 105 (1956).

Manuscript received April 14, 1958.

A Method for Determining the Sulfur Content of Wool

M. V. Glynn

Textile College, Gordon Institute of Technology, Geelong, Victoria, Australia

Abstract

The well-known method of wet combustion by means of a perchloric-nitric acid mixture has been applied to the determination of the sulfur content of wool. It has been shown to give results comparable with those obtained by standard microanalytical methods when applied to virgin wools of different qualities and to wool modified to contain the more resistant monosulfide linkage of lanthionine.

Introduction

Owing to the importance of sulfur in the reactivity of wool keratin, determination of the sulfur content of wool is of considerable interest. Tests at present available for this purpose include the Carius method—digestion for several hours; the Benedict Denis method [1]—a lengthy procedure leading to slightly low results; standard microanalytical methods—requiring specialized technique; and methods involving fusion with sodium peroxide—usually requiring special equipment and involving the possibility of incomplete oxidation. In view of these considerations it would seem that a need exists for a simpler, more rapid method, preferably involving no special equipment.

Wet combustion by means of perchloric-nitric acid digestion is a simple, rapid method which has been used successfully in determining the sulfur content of materials such as rubber [5, 11, 7, 6] and wood [2]. When Barritt [1] applied the method to wool, however, he was unable to obtain quantitative results. Thus, after the sample was boiled for 1 hr. in a Kjeldahl flask, sulfur recoveries of 57.8%, 75.3%, and 76.4% were obtained, while boiling under reflux for various times gave recoveries of 83.5% (2 hr. boiling), 92.2%, 96.0% (10 hr.), and 95.3% (20 hr.).

More recently, Hamlin [4] and Smith [10] have claimed that complete oxidation of wool is possible, but they give no results to indicate the percentage sulfur recovery. Smith, however, has stated that, in perchloric-nitric acid digestion, all the sulfur in organic compounds, except that originally present in elemental form, is retained as sulfuric acid. Bethge [2] obtained 100% recovery from cystine by this method, and in this laboratory 100.5% recovery was obtained from a cystine-cysteine mixture. In this case, digestion was carried out below the boil for several hours in a Kjeldahl flask, until the reaction mixture changed from yellow to colorless, the sulfur being then determined gravimetrically as barium sulfate.

In addition to the sulfur present in cystine and other amino acids, wool has been shown by many workers to contain a small amount of sulfur of unknown nature. Schöberl [8] and Simmonds [9] refer to "hydriodic acid reducible sulfur," and the possibility of elemental sulfur cannot be overlooked. This, according to Smith, would lead to a loss of sulfur as volatile gas during perchloric-nitric acid digestion. As some of the results obtained by Barritt are too low to be accountable in terms of elemental sulfur, it would seem, in view of the results obtained from cystine, that they were due either to interference from the other components of the wool molecule or simply to the use of incorrect conditions.

It is the purpose of this paper to show that complete recovery of sulfur from wool is possible by means of perchloric-nitric acid digestion and that the technique involved is simple, comparatively rapid, and able to be carried out with equipment normally found in a laboratory concerned with wool.

Materials and Methods

Wool

A bulk sample of Comeback 58's was prepared by removal of the fiber tips and purification of the root ends. This was effected by ether extraction for 4

hr. in a Soxhlet apparatus, followed by rinsing in several changes of distilled water. The wool was then allowed to come to equilibrium at 21° C. and 65% RH. Part of this wool was used in the preliminary work, the remainder being divided into smaller samples for chemical modification.

In addition, samples covering a range of different qualities were prepared, purified, and conditioned as above.

Modified Wool

Samples of modified wool were prepared by treatment with the following: (a) boiling distilled water for 1 hr., (b) 0.1 *N* caustic soda at 21° C. for 24 hr., or (c) boiling 0.65% potassium cyanide for 30 min. [4].

In each case the liquor/wool ratio was 100/1 and treatment was followed by thorough rinsing in distilled water. The samples were then conditioned as above.

Digestion Solution

Throughout the work, a mixture of equal parts (vol./vol.) 72% perchloric acid (AR) and concentrated nitric acid (AR) was used.

Digestion

Following the determination of a minimum liquor/wool ratio, 0.3-g. (conditioned weight) samples were digested with 10-ml. aliquots of the digestion solution. In the preliminary work, digestion was carried out in a Kjeldahl flask to a natural color-change end point (yellow to colorless). In all subsequent work, potassium dichromate indicator (Smith 1953)—5 ml. 0.1 *N* solution—was added, giving a green-to-orange end point, and, except where otherwise stated, digestion was carried out in a Soxhlet apparatus.

Sulfur Measurement

After cooling, the reaction mixture was transferred to a beaker, where the sulfur was precipitated as barium sulfate and determined gravimetrically. The results are based on the oven-dry weight of the wool.

As a basis of comparison, sulfur determinations have also been carried out on each sample "after Zimmerman" [12] in the Micro-Analytical Laboratory of the Division of Industrial Chemistry, C.S.I.R.O., at the University of Melbourne.

Results and Discussion

In view of the results obtained by Barritt, it was first necessary to show that complete recovery of sulfur by perchloric-nitric acid digestion was possible. Following general practice, the wool was first treated in boiling solution until the yellow color disappeared, which required 10–15 min. As the results obtained were unsatisfactory, digestion was then carried out at lower temperature, approximately 150° C., several hours being required for the color change to occur. Under these conditions the end point was satisfactory, and it was possible to obtain complete oxidation of the sulfur to sulfuric acid, provided the liquor/conditioned wool ratio was higher than 25/1 (vol/wt.)—for the particular wool involved. Using a 30/1 ratio and the lower temperature digestion, a mean recovery of 101.5% sulfur—based on microanalytical results—was obtained, showing that complete recovery of sulfur from wool was possible by this method.

To be acceptable as a test method comparable with those already available, however, more rapid digestion was necessary. This could be effected most conveniently by boiling, but since the natural color-change had proved unsatisfactory as an end point in boiling solution, it was decided to use potassium dichromate as an indicator (Smith 1953). Added prior to digestion, this was found to give a sharp end point within 15 min.; the results of the test are shown in Table I. The use of an open vessel, however, created a possibility of loss due to spitting; to eliminate this possibility, tests were carried out by boiling under reflux. The results, however, were similar to those obtained by Barritt, the indicator showing that reaction was still incomplete after 20 hr. of boiling. This was undoubtedly due to the fact that the oxidation potential of the mixture was insufficient to completely oxidize the sulfur. It is well known that the oxidation properties of perchloric acid increase with increasing concentration, as would have occurred in the open Kjeldahl flask.

To prevent or at least minimize spitting, while allowing for an increase in concentration of the perchloric acid by distillation, tests were next carried out in a Soxhlet apparatus, digestion occurring in the flask while the fumes were collected in the extractor. The need for a fume cupboard was thus eliminated, and reaction was found to be again complete within 15 min. Results are shown in Table I.

TABLE I

Method	% Sulfur, by wt.
Microanalysis	3.42
Kjeldahl digestion	3.39, 3.40, 3.44
Soxhlet digestion	3.42, 3.45, 3.46

TABLE II

Wool quality	% Sulfur	
	Acid digestion	Microanalysis
32's	3.28, 3.32, 3.33	3.22
46's	3.17, 3.19, 3.23	3.05
50's	3.55, 3.56, 3.59	3.59
56's	3.56, 3.58	3.57
70's	3.83, 3.85, 3.87	3.81

TABLE III

Treatment	% Sulfur	
	Acid digestion	Micro-analysis
Water	3.19, 3.23, 3.23, 3.25, 3.29	3.12, 3.17
Alkali	2.37, 2.41, 2.44	2.44, 2.50
Potassium cyanide	1.82, 1.95, 1.96, 1.97, 1.99	2.01, 2.07

During the preliminary work it was observed that boiling for extended periods led to high results, in contrast to the low results obtained by Barritt after boiling for 1 hr. Although overtreatment can be avoided by the use of the dichromate indicator, it was decided to examine this aspect more fully. By means of the indicator it was possible to control the extent of excess treatment; a result of 3.59% was obtained when, after boiling to the color-change (approximately 15 min.), a further 10-min. boiling was given. As with all previous tests, the precipitate was allowed to stand overnight before filtration. In a second test, in which digestion was again carried out for approximately 25 min. but the time of standing before filtration was only 3 hr., a normal result of 3.41% was obtained. As 3 hr. is more than sufficient time for complete precipitation of barium sulfate, there appears to be, in addition to the regular precipitate of barium sulfate, an additional precipitate if digestion is prolonged and if the solution is allowed to stand overnight. The addition of hydrobromic acid [2] prior to the addition of barium chloride failed to prevent its formation, the cause and nature of which is still unknown. It is believed that the low results obtained by Barritt were due to loss of sulfuric acid during boiling.

In order to show that the method applied to wool of any quality and degree of modification, tests were made on different quality wools (Table II) and on modified wools (Table III).

The main aim in modification was to convert cystine to lanthionine and thus determine the ability of the oxidant to completely oxidize the sulfur of the more resistant monosulfide linkage to sulfuric acid. The results in Table III show that this can be done.

It would seem therefore, from the foregoing results, allowing for differences which must be expected from two such differing methods, that perchloric-nitric acid digestion does offer a simple and comparatively rapid method for the determination of sulfur in any sample of wool. It is an empirical method in which either boiling must be discontinued as soon as oxidation of the sulfur is complete or the precipitate is not allowed to stand longer than 3 hr. before filtration. It is suggested that in carrying out the test, both points be observed. While not disproving the idea that elemental sulfur is present in wool, the results obtained suggest that in general, the possible amount present would lie within the normal limits of experimental error.

Acknowledgments

The author wishes to thank the administrators of the Wool Industry Research Fund, Dr. W. Zimmerman of C.S.I.R.O. for his cooperation in the matter of sulfur determinations, and the staff of the Textile Research and Testing Department for helpful discussion.

Literature Cited

1. Barritt, J., *J. Soc. Chem. Ind.* **53**, 291 (1934).
2. Bethge, P. O., *Anal. Chem.* **28**, 118 (1956).
3. Cuthbertson and Phillips, *Biochem. J.* **39**, 7 (1945).
4. Hamlin, A. G., *J. Textile Inst.* **40**, T343 (1949).
5. Kahane, E., *Caoutchouc and Gutta Percha* **24**, 13548 (1927).
6. Kress, K. E., *Anal. Chem.* **27**, 1618 (1955).
7. Mackay, J. G., *J. Soc. Chem. Ind.* **49**, 233, 410 (1930).
8. Schöberl, A., *Milliand Textilber.* **33**, 4 (1952).
9. Simmonds, D. H., *Proc. Int. Wool Text. Res. Conf. Aust.* **C**, 65 (1955).
10. Smith, G. F., *Anal. Chim. Acta* **8**, 397 (1953).
11. Wolesensky, E., *Ind. Eng. Chem.* **20**, 1234 (1927).
12. Zimmerman, W., *Mikrochim. Acta* **40**, 162 (1952).

Manuscript received March 24, 1958.

Papers Presented—28th TRI Annual Meeting

Predicting Commercial Acceptance of a Fiber[1]

J. L. Barach, R. G. Stoll, and A. F. Tesi

Celanese Corporation of America, Charlotte, North Carolina

ONE OF THE most important problems facing the textile industry is the assessment of the commercial possibilities for the many modified or new fibers that are coming into the market. It is therefore quite appropriate to discuss the critical factors which contribute to the acceptance or rejection of a fiber by those who expect to use it; namely, the representatives of the various segments of this industry.

From an academic point of view, a new fiber, just as any other product, must find commercial acceptance either by moving into new markets or by replacing fibers already being used.

A critical analysis of this situation seems to leave a new basic fiber no alternative; it must capture part of the market already being held by other fibers. Fiber consumption statistics such as outlined in the March 1958 *Textile Organon*, pp. 69 and 72, show clearly that since 1941 overall poundage consumption has remained more or less stationary, while per capita consumption of fibers has dropped. For example, per capita consumption for 1957 was about 32.4 lb. This condition may have been brought about in part by the fact that a pound of fiber now results in more yards of fabric, due to less waste and higher strength. This trend is true for industrial as well as apparel and home furnishing fabrics. Consumption statistics also indicate that incremental growth made possible by entirely new and different applications has been quite small. A consideration of all facts available reveals that many areas are now being explored and that the next decade may show growth, particularly in the per capita consumption. Long range forecasts estimate this at 44 lb. per capita consumption 50 years from now. Some success may also accrue from the current attempts to capture a greater share of the consumer dollar for textiles, but this will take much time and considerable effort. The salesmen will be in the forefront of this effort, and the contribution of research in the creation of new fibers and the development men in the area of new process and applications will undoubtedly lead to greater fiber consumption. Nevertheless, to be practical and realistic in appraising where the possibilities for any new fiber lie today, one must take a conservative point of view.

In discussing the factors which influence the acceptance of a new or modified fiber into the commercial field where it will compete, the problem is quite different from predicting future usage of an existing fiber for which market data are already available. The assumption is made that the basic demand for fibers in apparel, home furnishings, and many industrial uses has already been met. In addition, it is assumed that while the population will grow, the usage of fibers will expand very little. The problem therefore resolves itself in determining how this new or modified fiber will fit in with—or possibly "nudge out"—existing fibers. In brief, a new or modified fiber must fit into the markets presently available for the sum total of fibers. Acceptance of a fiber is a game which involves the interactions that exist among various segments of the textile industry. In a broad sense, it is similar to the game the military strategists use in setting up the basis for military operations; the kind of game that Mr. John McDonald wrote about in *Fortune* some years ago when he discussed the strategy of the business world; the kind of game that John Von Neumann and Oskar Morgenstern talked about in their book "Theory of Games and Economic Behavior." It is the kind of game which, in theory at least, can be subjected to mathematical analysis, and if sufficient information

[1] Presented at the 28th Annual Meeting of the Textile Research Institute, New York City, March 14, 1958.

is known, will have a predictable outcome. And, perhaps fortunately, it is the kind of game where the players do not know all the factors which motivate the other principals.

When applied to the apparel and home furnishings phase of the textile industry, the game is played by several: the fiber producer, the textile manufacturer (the spinners, weavers, dyers, and finishers), the converter or more generally the finished goods merchant, and the cutter or other end use manufacturer. In the case of special groups such as the sweater manufacturer, the game is played by the sales yarn spinner, fiber producer, and finished goods merchant. In industrial products, the textile manufacturer, fiber producer, finished goods merchant, and consumer or user play the game.

With so many involved, it is quite apparent that the problem is to select the particular player who makes the decision which results in the purchase of fiber and to determine what influences him. To do so, it is necessary to determine the factors on which he bases this decision—the incentive he has—and see if it can be influenced. The business of selecting fibers then is a game for three or four people or groups of people who are essentially independent of each other, and what needs to be done is to find if a pattern exists behind the moves the players make. This analysis may also give the answer as to why many development programs stop for no apparent reason and, in spite of valiant efforts, die on the spot.

What are the major objectives of each of the players? It is quite apparent that a common incentive is to make money. It is also clear that the finished goods merchant wants to be able to sell or offer something new. The fiber producer wants to sell fiber. The textile manufacturer, which includes the spinner, weaver, dyer, and finisher, wants to make a higher profit than he is able to with his present products, or at least make no lower profit.

TABLE I. Factors Influencing the Finished Goods Merchant

Sales appeal of finished fabrics
Minimum performance requirements
  Durability and general performance
  Ease of care properties
  Colorfastness

Factors Influencing the Textile Manufacturer

Ease of spinning
Ease of knitting
Ease of weaving
Ease of dyeing and finishing

In addition, he may wish to diversify his services by expanding into other areas of effort.

This basic problem has been studied many different times. In fact, Mr. Corey of the Harvard Business School has outlined the factors which help determine the willingness and incentive to make and sell a new end product in his book "The Development of Markets for New Materials." Incidentally, the book includes a study of Fiberglas and its introduction to the textile market. He says that incentives can be included in the answers to these three questions:

A. Will taking on the new product require him to make a substantial change in the production organization and invest significant amounts of capital in new plant facilities?

B. Will sales of the new product substitute for sales of the existing product to present customers?

C. Will making and selling the new product give the manufacturer a competitive advantage, enabling him to increase his share of the market in which he operates or to establish himself in some new market?

The approach herein outlined we believe is somewhat more detailed and easier to use. Examination indicates that those who will be most influential and will be in the best position to make a decision regarding the acceptance of a new fiber will be the finished goods merchant and the textile manufacturer. Table I is an overall outline of the major divisions into which these factors which influence these two segments of the textile industry can be divided. In most cases, while the merchant of the finished goods may not actually purchase the fiber, it is his decision which will lead to the purchase being made. We should therefore be most interested in learning his wants and determining his needs. These are listed in some detail in Table II.

These are the rules by which the finished goods merchant is playing this game. Special attention is called to the "minimum performance requirements," since it is here that for the first time a possibility exists for a mathematical approach to the problem of predicting the commercial acceptance of a new fiber. Mr. Purnell H. Benson of Drew University treated one aspect of this in some detail in a paper entitled "Optimizing Product Acceptability Through Marginal Preference Analysis," presented at a Rutgers University conference on quality control last year. There Mr. Benson pointed out that any

combination of qualities which a consumer or customer may rank will reach an optimum at some point, and if enough information is available, it will be possible to draw a curve which will represent this acceptance. For the minimum performance standards under discussion, an exponential function such as that shown in Figure 1 would be realistic. A single critical factor below a certain level which is completely unacceptable to the customer or consumer may prevent acceptance on any basis. Above a certain level, further improvement in any factor will not result in increased acceptance by the user. Figure 1 illustrates this; if taken in a general sense, it might apply to strength, elongation, colorfastness, washfastness, soilability, or any of the other factors which can be measured on a fabric or product. This type of function may be applied more generally to the requirements of the finished goods merchant in determining his level of acceptance. However, it is particularly pertinent to the minimum performance shown earlier. If a minimum performance is below a certain level, the merchant would not accept a fabric at all. If it meets or exceeds his minimum performance level, the other group of factors listed under sales appeal will have the major influence on his decision. To say it another way, a property that is in excess of a safe margin over that required is not necessarily an incentive to change, unless there exists a real demand or the advantage can be promotionally exploited. Everyone has seen a stylist or designer look at a fabric, like it for color and hand, and then pop it with his thumbs. This means it failed to meet his personal minimum strength performance level.

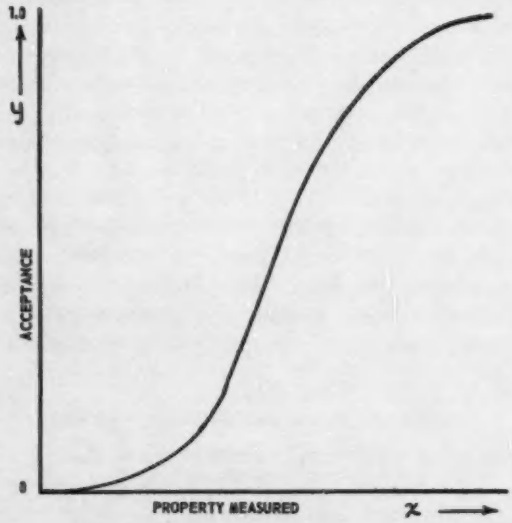


Fig. 1. Acceptance function; $y = 1 - e^{-bx}$.

The simplest mathematical way to take account of the interaction which exists among these factors and still meet the requirements of no further increase after a certain level has been reached and complete rejection if the quality is below minimum requirements would be to set up functions for each of the general groups and multiply them. This is of course an oversimplified approach and, as might be suspected, of only limited usefulness. Work of the type discussed by Mr. Wetmore of Du Pont at an AATT meeting in New York City and published in April 1958 *Modern Textiles*, p. 67, demonstrates

TABLE II. Factors Influencing Acceptance by the Finished Goods Merchant

Sales appeal of finished fabric
- Immediate market demand exists
- Consumer wants: Relative to style
  Relative to performance
- Provides uniqueness: Style
  Performance
- Provides versatility of end use
- Penetration—Diversification
  Styling
  Applications
- Favorable cost-profit ratio
- Fits long range market trend
  Relative to style
  Relative to performance

Minimum performance requirements
- Durability and general performance
  - Strength
  - Wear resistance
  - Pilling resistance
  - Chemical and photochemical resistance
  - Glazing and heat resistance
  - Fire resistance
  - Sewability and seam strength
  - Ease of pressing and forming
  - Soil resistance and ease of soil removal
- Ease of care properties
  - Dimensional stability
  - Wrinkle resistance (dry and wet)
  - Crease retention—pleatability
  - Ease of laundering and drying
  - Ease of ironing
  - Appearance after washing and drying
  - Retention of appearance
- Colorfastness
  - Washfastness
  - Lightfastness
  - Miscellaneous fastness properties (fume fading, perspiration, whiteness retention)

that the results possible by the application of electronic computers to a somewhat related problem should point the way toward an orderly approach to problems of the type under consideration.

The next and second most important group of factors includes those which influence the manufacturer of a textile product, and these are listed in Table III. They are extensions of the physical parameters usually considered, but to a marketing man they seem more sophisticated and pertinent. If the answer to this portion of the assessment is unfavorable, the changes are that the fiber in question will never "get off the ground."

What about the third player in the game—the fiber producer? The rules by which he operates assume that he has an approximation of the fiber selling price and that the decision in question is whether or not to make the fiber.

The first price represents the minimum which a fiber producer would consider. This is composed of his base material cost plus the processing cost plus profit. The second is the maximum the industry will pay for this fiber in competition with others available. It is made up of spinning costs and profit, plus weaving costs and profit, plus dyeing and finishing costs and profit, plus weaving costs and profit, plus converter cost and profit. If the maximum the industry will pay is below the minimum the fiber producer could consider, obviously the fiber will not be made for long. If the reverse is true, a market is assured. If it were really as simple as this, there would be no need for the complicated assessment discussed here. However, these facts are believed to be basic to a real understanding of the problem.

TABLE III. Factors Influencing Acceptance by the Textile Manufacturer

Spinner
Fiber cost incentive
Uniformity of raw material supply
Stability of raw material price
Yarn manufacturing costs incentive
Spinnability of fine yarn counts
Appearance factor
Adaptability to various spinning systems
Weaver or knitter
Yarn cost incentive
Adaptability to present equipment
Technical suitability for processing
Manufacturing costs incentive
Versatility of useful ranges in yarn sizes
Dyer and finisher
Dyeing and finishing cost incentive
Adaptability to present equipment
Versatility of shade range including cross, reserve, and union dyeing possibilities
Ease of meeting quality standards
Ease of meeting good fastness requirements
Possibility of finishing for various hands

It is axiomatic that the study by the fiber producer should be done as early as possible and, if necessary, redone several times to reassess the possibility of commercial acceptance. This will undoubtedly prevent some very expensive mistakes; considering the amount of capital which a fiber producer must invest before he makes a new fiber, the study is a very inexpensive management tool.

In order to illustrate an application of this method, high tenacity rayon staple has been chosen. This fiber has been made by a number of fiber producers and is on the market at the present time; its price has been established. However, commercial acceptance is still in doubt. Let us try to play the game and hope it corresponds to the reality which might exist if a high tenacity rayon staple with the assumed properties were placed into the present textile apparel and home furnishings market.

To make this realistic, it is necessary to describe the properties of this fiber. It will have a tenacity of 3.5–4 g./den. and an elongation of approximately 25%. It can be crimped sufficiently to process on normal spinning equipment and is available in 1.0, and perhaps up to 3.0 den./filament. All dyes which are used with the present textile rayon will dye the fiber, but the rate of dye absorption will be somewhat reduced. Resin stabilization or the Sanforized process is required to produce fabrics stable to home laundering conditions such as those specified for automatic wash and wear. The assumption will be made that an unlimited amount of this fiber at 40–45¢/lb. is available; since it is replacing another fiber, it is not going into a tight market situation. It will further be assumed that the problems which today plague the converter and manufacturer of greige goods—very large swings in the business cycles coupled with huge inventories of specific fabrics and unrealistic pricing to clean out

TABLE IV. Rating Scale for Incentive Factors

Large incentive to change	+2
Little incentive to change	+1
No choice	0
Little resistance to change	−1
Large resistance to change	−2

TABLE V

Incentive to Change.....in.....

To H. T. Rayon

Textile Manufacturer

	Large incentive		No choice	Large resistance	
	+2	+1	0	−1	−2
Spinner					
Fiber cost incentive					
Uniformity of raw material supply					
Stability of raw material price					
Yarn mfg. costs incentive					
Spinnability of fine yarn counts					
Appearance factor					
Adaptability to various spinning systems					
Weaver or knitter					
Yarn cost incentive					
Adaptability to present equipment					
Technical suitability for processing					
Manufacturing costs incentive					
Versatility of useful ranges in yarn sizes					
Dyeing and finishing					
Dyeing and finishing cost incentive					
Adaptability to present equipment					
Versatility of shade range including cross, reserve, and union dyeing possibilities					
Ease of meeting quality standards					
Ease of meeting good fastness requirements					
Possibility of finishing for various hands					

the warehouse—will not influence the answers. Normal promotional support presumably is available.

The factors which influence the two principal players (the finished goods merchant and the textile manufacturer) as listed in Tables II and III have been rated for high tenacity rayon in comparison with the fibers believed to be directly competitive—cotton and rayon. These were rated for specific applications believed most representative, including

a. replacement of cotton portion in cotton/Dacron [2] and cotton/Orlon [2] blended light weight fabrics,

b. replacement of cotton in fine cotton fabrics such as voiles, lawns, etc.,

c. replacement of cotton in broadcloths, print cloths, and sheetings,

d. replacement of either regular or extra strength rayon in men's outerwear, sport shirts, and children's wear, and

e. replacement of rayon in women's dresses, suitings, and skirts.

[2] Du Pont trademark.

This rating is based on a scale shown in Table IV and is designed to indicate the incentive a finished goods merchant or textile manufacturer might have to change to the new fiber (high tenacity rayon staple) or the resistance to this change he may be expected to voice.

By use of the factors shown in Tables II and III, the applications were rated by using rating sheets such as those shown in Tables V and VI; a summary of results is shown in Tables VII and VIII. Three groups are shown: the sum of the positive or incentive factors, the sum of the negative or resistance factors, and the arithmetic average (including zeros) of all factors rated. The analysis of this is more easily accomplished by viewing graphs made for three applications as shown in Figures 2 and 3. Choice of this graphical method presentation was dictated since, in any case where any factor is negative, the specific factor must be examined to determine if this negative will rule out the application or if sufficient incentive exists elsewhere to overbalance the negative.

The interpretation of these graphs is an area where

we are still quite unskilled. Certain factors are quite clearly shown to be important in a positive sense—for example, those grouped as "Better Sales Appeal." Others, such as performance factors, are more important in a negative sense. Nevertheless, there may be among them positive factors such as exceptional wear durability, colorfastness, or ease of care which can be successfully promoted. Those relating to manufacturing by the spinner, weaver or knitter, and dyer and finisher are important both positively and

TABLE VI

Incentive to Change.....in.....

To H. T. Rayon

Finished Goods Merchant

	Large incentive		No choice	Large resistance	
	+2	+1	0	−1	−2
Sales appeal of finished fabric					
Fits long range market trend					
Relative to style					
Relative to performance					
Immediate market demand exists (consumer wants)					
Relative to style					
Relative to performance					
Provides uniqueness of					
Style					
Performance					
Provides versatility of end use					
Penetration—diversification					
Styling					
Applications					
Favorable cost-profit ratio					
Minimum performance requirements					
Durability and general performance					
Strength					
Wear resistance					
Pilling resistance					
Chemical and photochemical resistance					
Glazing and heat resistance					
Fire resistance					
Sewability and seam strength					
Ease of pressing and forming					
Soil resistance and ease of soil removal					
Ease of care properties					
Dimensional stability					
Wrinkle resistance (dry and wet)					
Crease retention—pleatability					
Ease of laundering and drying					
Ease of ironing					
Appearance after washing and drying					
Retention of appearance					
Colorfastness					
Washfastness					
Lightfastness					
Miscellaneous fastness properties (fume fading, perspiration, whiteness retention)					

negatively depending on the particular application. Experience is needed to give the final answer, but the likelihood of acceptance in the applications selected rated in order of decreasing acceptance are:

1. Replacement of cotton by H. T. rayon in fine cotton goods—fair chance for acceptance.

2. Replacement of either regular or extra strength rayon in men's outerwear, sport shirts, and children's wear—fair–poor chance for acceptance.

3. Replacement of cotton in cotton/Dacron or cotton/Orlon fine goods—fair–poor chance for acceptance.

4. Replacement of cotton in broadcloths, print cloths, and sheetings—poor chance for acceptance.

5. Replacement of rayon in women's dresses, suitings, and skirting—poor chance for acceptance.

In judging the value of this approach, it should be emphasized that one specific price range was assumed. A change in price, whether accomplished by a change in list price or by promotional and advertising assistance, may have a disproportionate effect on the incentives all along the line and thus on the results.

TABLE VII. Summary of Incentive to Change to High Tenacity Rayon

	Incentive to change from								
	Cotton in Dacron/cotton and Orlon/cotton			Cotton in fine cotton goods			Cotton in broadcloths, print cloths, sheetings		
	Total +pts.	Total −pts.	Avg.	Total +pts.	Total −pts.	Avg.	Total +pts.	Total −pts.	Avg.
Sales appeal of finished fabric	1	1	0	3	1	+0.21	0	2	−0.22
Minimum performance requirements	1	0	−0.10	1	1	0	0	1	−0.13
Ease of care properties	0	0	0	0	0	0	0	0	0
Colorfastness	0	0	0	0	0	0	0	0	0
Spinner	6	0	+0.85	6	0	+0.88	4	1	+0.51
Weaver and knitter	1	0	+0.20	1	0	+0.23	0	0	0
Dyer and finisher	1	0	+0.17	0	0	0	0	0	0
Totals	10	1	+1.12	11	2	+1.32	4	4	+0.16

TABLE VIII. Summary of Incentive to Change to High Tenacity Rayon

	Incentive to change from					
	Regular rayon in men's outerwear, sport shirts, and children's wear			Regular rayon in women's suitings, dress goods, and skirts		
	Total +pts.	Total −pts.	Avg.	Total +pts.	Total −pts.	Avg.
Sales appeal of finished fabric	2	1	+0.10	0	1	−0.10
Minimum performance requirements	2	0	+0.21	0	0	0
Ease of care properties	2	0	+0.3	1	0.14	+0.14
Colorfastness	0	0	0	0	0	0
Spinner	1	1	0	0	1	−0.14
Weaver and knitter	1	1	0	0	1	−0.2
Dyer and finisher	0	0	0	0	0	0
Totals	8	3	+0.61	1	3	−0.30

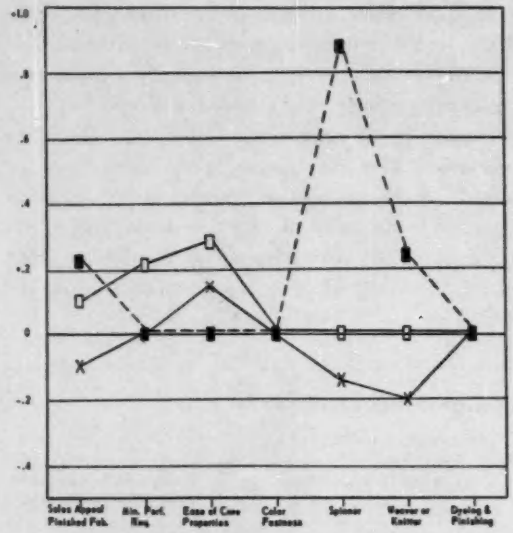


Fig. 2. Incentive factors for change to high tenacity rayon. Incentive to change from:

× Regular rayon in women's suitings, dress goods, and skirts to H.T. rayon.

□ Regular rayon in men's outerwear, sport shirts, and children's wear to H.T. rayon.

■ Cotton in fine cotton goods (100% replacement) to H.T. rayon.

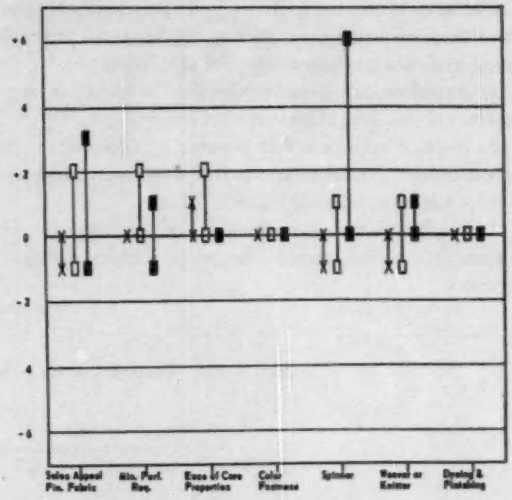


Fig. 3. Incentive factors for change to high tenacity rayon. Incentive to change from:

× Regular rayon in women's suitings, dress goods, and skirts to H.T. rayon.

□ Regular rayon in men's outerwear, sport shirts, and children's wear to H.T. rayon.

■ Cotton in fine cotton goods (100% replacement) to H.T. rayon.

Summary

In summary, a new approach to the difficult problem of predicting the possible commercial acceptance of a new basic fiber has been presented. Factors such as processing and user performance have been listed; in addition, the even more important incentive factors such as sales appeal and its influence on market acceptance have been included. It has been shown that the finished goods merchant plays the most important role, since he integrates the incentives of the other players in the game, and he answers the question as to what the market wants. It is here that the best poker player with the most knowledge of the cards held by his opponents will be in the best position to make the most profitable moves.

Bibliography

"A Theory of Strategy," John McDonald, *Fortune Magazine* **39**, 100–110 (June 1949).

"The Development of Markets for New Materials," E. Raymond Corey, Division of Research, Graduate School of Business Administration, Harvard University (1956).

"Optimizing Product Acceptability Through Marginal Preference Analysis," Purnell H. Benson, Drew University—published in Rutgers University report of September 6, 1957, conference "Quality Control and The Consumer."

"Introduction to Operations Research," C. W. Chuchman, Wiley and Sons (1957).

Textile Organon, March 1957.

Recent Advances in the Industrial Use of Synthetic Fibers[1]

J. M. Swanson

Industrial Products Research, Textile Fibers Department,
E. I. du Pont de Nemours & Company, Inc., Wilmington 98, Delaware

Abstract

End-use research and development work on improved yarns, tailored to meet specific industrial needs, are broadening the use of synthetic fibers in industrial applications. Examples include the use of nylon for tires, which is expanding due to its inherent performance advantages over rayon and the development of techniques for utilizing improved nylons to best advantage; use of "Dacron"[2] polyester fiber for V-belts, where techniques for handling adhesion and belt dimensional stability problems have been developed; and use of nylon in vinyl-coated fabrics, where a new adhesive has been formulated which gives good bonding with both plastisol-coated and laminated structures. Continued research and development may be expected to expand further the industrial use of synthetic fibers.

Introduction

Until fairly recently, when people thought of synthetic fibers it was generally in conjunction with apparel uses, such as hosiery, lingerie, blouses, and dress fabrics. Over the past several years, however, an increasing demand for synthetic fibers in industrial applications has developed. This trend has been accelerated by the efforts of synthetic fiber producers to tailor their products to fit specific needs, augmented by work on solving the processing and performance problems which inevitably arise when any material is first put to use in a new field.

The du Pont Textile Fibers Department has been quite active on this type of work, which has come to be called "end-use" research. Where industrial fiber applications are involved, work is carried out at the Industrial Products Research Laboratory, which was started in 1954.

The work done in this laboratory is not customer service, but research in the full sense of the word. The program includes both theoretical studies and practical experimentation. In fact, it has proven necessary to penetrate quite deeply into the fundamentals of the processing and use conditions to which fibers are exposed. For example, in the tire field extensive studies have been carried out on the role of both the fiber and the elastomer in tire performance, on the mechanism of tire failure, on tire ride performance as it relates to the automotive suspension system, and on tire strain analyses, utilizing both experimental and mathematical techniques. A comparable approach is being followed in programs on major new uses as well as on other existing markets.

The following presentation is a review, primarily from the technical standpoint, of some of the advances in the industrial use of synthetic fibers, including our work in the field where pertinent.

[1] Presented before the 28th Annual Meeting of the Textile Research Institute, New York City, March 13, 1958.

[2] Registered Du Pont trademark.

Recent Developments

Nylon Reinforcement for Tires

Nylon is rapidly gaining favor as a reinforcing fiber for tires. In 1957, about 85 million pounds of nylon were used in passenger, truck, airplane, and off-the-road tires. This represents an increase of 35% over 1956 figures, and about one-third of the total tire yarn market, expressed in nylon units. The reason for this trend lies in the performance advantages of nylon tires compared with rayon. We have explored this subject in considerable detail; summarized below are the results of two key performance comparisons which have led us, as producers of both fibers, to conclude that the swing towards nylon will continue.

TABLE I. Crown Impact Endurance Test Results

	Impacts to failure $\times 10^{-3}$
Rayon	50–150
Nylon	300–500

TABLE II. Taxi Test Data

	Nylon	Rayon
Test A		
Total tires	27	28
Impact breaks		
Original tread	0	1
End of test	2	16
Test B		
Total tires	78	78
Impact breaks		
Original tread	1	9
End of test	9	47
Test C		
Total tires	100	100
Impact breaks		
Original tread	1	6
Test D		
Total tires	59	59
Impact breaks		
Original tread	0	4

Nylon tires offer outstanding bruise resistance. This accounted for the early use of nylon in airplane and earthmover tires. The advantage of nylon over rayon tires in this respect is readily detectable in both laboratory testing and actual use. For laboratory work we have found a "crown impact endurance" wheel test to be a particularly useful gauge of tire bruise resistance. The crown impact endurance test involves running a tire to failure at 35 mph, at normal inflation and 15% overload, over a 3.5-in. long plunger 1.25 in. in diameter, mounted at an angle to the test wheel surface. As the tire runs over the plunger the tread is deflected about 2.5 in. Successive blows occur at different points on the tire.

With this test, different ratings are obtained with different fibers and with modifications in tire design. In Table I are shown typical results obtained on laboratory-built nylon and rayon tires. Tires reinforced with "super" rayons survived 50,000–150,000 impacts, whereas nylon tires ranged from 300,000–500,000 impacts. These tires were of the same design and were built with the same rubber stocks. They differed only in the type and amount of fiber.

TABLE III. High Speed Endurance 8.00 × 15 Tires

Reinforcing fiber	No. tires tested	No. unfailed 3000 mi.	Average mileage*
Nylon	31	25	2860
Rayon	30	8	1660

* Tests of unfailed tires stopped at 3000 mi.

The nylon tires contained about 1.8 lb. of cord per tire, whereas the rayon contained about 3 lb. of cord, approximating commercial practice.

These results, of course, are laboratory experiments, and one immediately asks about their significance in terms of actual service performance. Accordingly, we have carried out a series of taxi tests in which commercial tires were run through the original tread and were then retreaded repeatedly. Some of the results obtained are shown in Table II. It is clear that in actual service the commercial nylon tires also showed a superiority in bruise resistance. This superiority showed up on the original tread and persisted through repeated retreads.

A second advantage of nylon reinforced tires is found in high-speed, high-temperature performance. This can be readily demonstrated by laboratory wheel tests. In a standard step-speed test, where tires are run with a step-wise increase in speed after an initial break-in period, it is generally agreed that nylon tires will tolerate about 10 mph higher speed. Perhaps a more significant test is the tire behavior at constant high speed. We have made such comparisons with a high-speed endurance test in which tires are run at 75 mph under a 20% overload to failure or 3000 miles, whichever comes earlier. The results obtained are given in Table III; 25 out of 31 nylon tires survived 3000 miles for an average mileage of 2860 miles, whereas only 8 out of 30 rayon tires survived the test, giving an average mileage of 1660. These were all laboratory-built tires with the same basic design and same rubber stocks as described previously. In a similar comparison of commercial tires, the average mileages were essentially the same: 2740 miles for nylon tires versus 1775 miles for rayon. In other tests where all tires were run to failure, nylon tires gave an average mileage of 5500 compared with 1700 miles for rayon.

It appears that the superior high-speed performance of nylon stems in part from the fact that it shows a linear contraction with increase in tempera-

TABLE IV. Cord Strength Loss in High Speed Endurance Test

Reinforcing fiber	% Cord strength* loss/3000 miles
Type 700 nylon	5
"Super" rayon	15

* Outer ply at shoulder of tire.

ture, so that as the tire heats up the cords pull in and take some of the strain off the rubber. Thus, the fiber directly influences tire behavior at high speed, although the actual point of tire failure under short runs at high speed is usually in the elastomer, manifested as tread loss, or "chunking."

Under conditions of prolonged running at somewhat lower speeds, particularly in truck tires, sufficient cord degradation may occur to cause actual carcass failure. This is sometimes referred to as "heat fatigue" failure in truck tires. Here again nylon shows up to advantage, as can be seen by dissecting tires that have been run at high speed and observing the cord strength loss in the outer plies of the shoulder of the tire, where most heat is developed. This is seen in Table IV, where data obtained on Type 700 nylon and "super" rayons are compared in terms of cord strength loss per 3000 miles in the high-speed endurance test which was described earlier. These data show that the rate of strength loss is far less with nylon. This effect is probably tied in with a greater resistance to heat degradation coupled with lower hysteresis at elevated temperatures shown by nylon, as described by G. D. Mallory at last year's meeting of the Textile Research Institute.

With this background on the chief incentives for using nylon in tires, we shall next consider some of the problems that have had to be solved in order to capitalize on its advantages. There have been major problems, as might be expected at a time of transition. This was demonstrated previously in the shift from cotton to rayon for tires. All who were involved with tires at the time recall the problems of fatigue, adhesion, and processing that had to be solved before rayon could be utilized to full advantage. Nylon has also had problems, although of a different kind. Essentially all of the problems stemmed from a common source—the relatively low fiber modulus. The fiber modulus is determined by the same features of polymer molecular structure that account for the flex and bruise resistance shown by nylon at a high level of fiber strength. The nylon molecules are very flexible; although they crystallize, they do not freeze into a highly crystalline structure. As a result, nylon is a supple fiber, but its tensile modulus is significantly below that of cotton or rayon. This gave rise to growth problems with early tires. Another closely allied problem was that of tire cost. Ways had to be found to avoid the necessity of overbuilding nylon tires, that is, using more fiber than was needed for durability, to bring growth under control. Also associated with modulus were the problems of a marginally higher treadwear and different "tire aesthetics." This term refers to the performance characteristics of tires which the driver judges subjectively, such as steerability, ride performance, and the transient set which a tire takes when it stands under load overnight. This transient set is also referred to as "flat spotting" and is more pronounced with nylon than rayon tires. It gives rise to a change in ride characteristics when a vehicle is started up after standing, and is detectable on a smooth road for a short distance.

Early in the work on nylon tires, which goes back, incidentally, to the early '40's, it was shown that by stretching nylon in cord form and heat setting it in the stretched state, the modulus of the cord structure could be increased without significant sacrifice in fatigue. Furthermore, although the cord denier was reduced by stretching, breaking strength actually increased, so that more strength was realized from a given weight of fiber. This is illustrated in Figure 1, which shows how cord growth (the inverse of modulus) decreases and breaking strength increases with increase in the amount of stretch put into the cord by the hot stretching treatment. With the stretched cord, at the same fabric end count, stronger, lower-growth tires could be built with a reduction in cord content corresponding to the percent of net stretch. A further reduction in cord content could

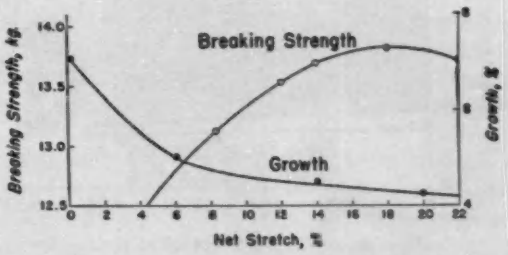


Fig. 1. Effect of hot stretching on cord properties.

be realized by decreasing end count to the level dictated by carcass durability requirements, since growth could be brought under control without overbuilding the tire. Obviously, hot stretching represented an attractive route to the improved utilization of nylon.

Tire manufacturers pursued this line of attack, combining the stretching with a drying step which followed normal adhesive application. The dip-stretching process was thus evolved which permitted the manufacturer to get the growth problem under reasonable control and to lower tire cost. However, further improvement was desired, and a problem developed with stretched cord because the simple one-step stretching treatment proved inadequate to do a satisfactory setting job. The stretched cord tended to shrink when freshly cured tires were removed hot from the mold, as occurs in modern high-speed curing procedures.

More recently, three new developments have come about which open the route to virtual elimination of growth as a problem, circumvention of the dimensional stability problem, and further improvements in cost, treadwear, and flat spotting. These are: (1) multiple-step stretching; (2) an improved nylon which is stronger, tougher and more resistant to degradation during prolonged exposure to high temperatures (this product has permitted attainment of a higher degree of stretch in the cord form); (3) "post inflation," which is a post-curing treatment for tires, involving inflation of the hot tire with air and subsequent cooling in the inflated state.

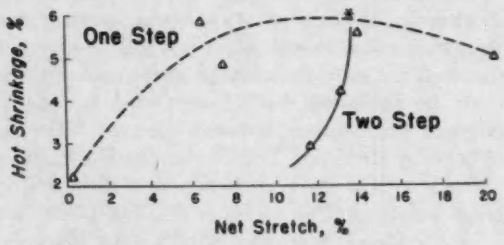


Fig. 2. Effect of multiple-step stretching.

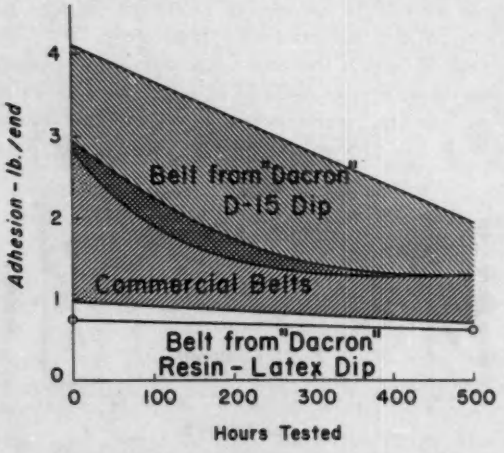


Fig. 3. Belt adhesion in dead weight testing.

Multiple-step stretching involves a first step in which the cord is highly stretched followed by one or more annealing steps in which the cord is exposed to further heat setting while it is allowed to shrink a small amount. This has a pronounced effect on residual cord shrinkage, as is shown in Figure 2, where cord shrinkage at curing temperature is plotted against net stretch. The dotted curve shows the properties of one-step stretched cord. If a cord which has been stretched in one step is exposed to a second annealing step, the relationship between shrinkage and stretch follows the solid line. Thus two-step stretching gives a more stable cord at a high level of stretch.

The combination of this multiple-step stretching treatment; the improved yarn, specifically tailored for the process; and "post inflation" represents an important advance in nylon tire technology.

At the present time, the principles for handling the major problems with nylon and capitalizing on its advantages appear to be pretty well in hand. Further advances may be anticipated from new leads which are developing. Reduced ply tires, for example, offer a route to cooler running, softer riding tires for both passenger and truck use, in which still better utilization of nylon's strength and toughness can be realized. Other work has pointed up op-

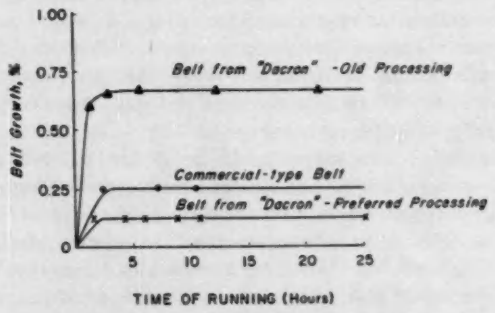


Fig. 4. Belt growth (dead weight testing).

portunities for further improvements in tire aesthetics, by proper choices of the elastomer and tire design to go with a given fiber. All told, major technical progress has been made which will permit expanded use of nylon for tires in the future.

Non-Tire Applications

"Dacron" Polyester Fiber in V-Belts

The physical properties of "Dacron" suggest that it should be an excellent reinforcing fiber for V-belts; however, two technical problems have retarded its use: adhesion and dimensional stability. Adhesion with conventional aqueous-base adhesives was questionable. Solvent-base isocyanate adhesives gave relatively good adhesion, but few users were able to handle solvents safely in their dipping and drying operation. An aqueous-base adhesive was needed to permit widespread commercial use of "Dacron." In the fall of last year a new aqueous adhesive formulation for "Dacron," coded D-15, was announced by du Pont after extensive research. This formulation utilizes an aqueous dispersion of a phenol-blocked isocyanate in combination with a suitable latex. D-15 gives an excellent level of adhesion between "Dacron" and selected GRS and neoprene belting stocks. Data in Figure 3 show the level of adhesion obtained with a conventional aqueous dip and with D-15 in combination with various stocks, compared with the range of adhesion found with commercial belts. Although not yet universally applicable to all elastomers, this formulation is being utilized with good success commercially.

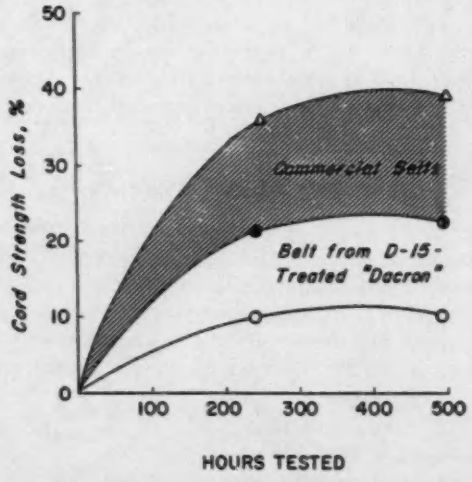


Fig. 5. V-belt cord strength loss (dead weight testing).

Progress has also been made on the dimensional stability problem. This problem was twofold: shrinkage of the belt upon removal from the mold, which gave rise to variable belt size; and belt growth, or increase in belt dimensions with service, which prevented its use in services where growth tolerances are tight. A practical solution to this problem has been worked out for automotive and small industrial belts. This involves modified cord stretching and curing procedures similar to the techniques just described in the discussion on tires. The effect of these processing changes, in terms of belt growth, is shown in Figure 4. This shows belt growth versus running time for a commercial-type belt, compared with a reinforced belt of "Dacron" polyester fiber produced under the processing conditions now recommended and under conditions previously employed.

These advances in adhesion and dimensional stability have opened the door to fuller utilization of the strength, toughness, and moisture resistance of "Dacron" in belting. Belts with "Dacron" have been shown to offer higher impact resistance and greater strength per unit of cross section. In addition, belt strength retention with service is better than current commercial products. This has been shown by exercising belts for various lengths of time, dissecting them to remove the cords, and determining the cord strength loss with service. Typical results are seen in Figure 5, which compares the strength loss found for representative commercial belts and belts reinforced with D-15-treated "Dacron."

Du Pont's work in this field is continuing with emphasis on the application of the above principles to the larger industrial belts.

Coated Nylon Fabrics

The market for coated nylon fabrics has grown rapidly over the past five years, as can be seen from Figure 6. The reason is that these structures offer a low-cost route to lightweight, durable protective coverings. A comparison with conventional treated cotton duck of about the same level of grab strength is shown in Table V.

With vinyl-coated fabrics, adhesion represented a barrier to expanded markets. In uses where severe flexing was encountered, separation of the coating was a common occurrence. Only in the past year or so have vinyl plastisol-coated nylon fabrics been

placed on the market which have shown adequate adhesion for this type of service. Laminated structures have been limited to open-mesh fabric sandwiched between two sheets of vinyl film. This construction was required to achieve bonding of vinyl-to-vinyl by strike-through in the holes of the fabric. Strong, tightly woven fabrics could not be satisfactorily laminated.

Du Pont has carried out research on this problem and recently developed an adhesive formulation coded NVD. This adhesive is not only applicable for plastisol coating, but can also be used to laminate vinyl films to both tightly-woven and open-mesh nylon fabrics. The laminated products show an excellent level of adhesion in the same range as the coated materials. Representative adhesion values for commercial and experimental vinyl-nylon fabrics are shown in Table VI.

This development has opened up a route to a new class of high-quality vinyl-nylon protective coverings.

TABLE V. Properties of Coated Fabrics

	Coated nylon	Treated cotton duck
Fabric weight, oz./yd.²		
Base fabric	5	24
Coated fabric	17	34
Grab strength, lb.		
Warp	400	375
Filling	380	300
Tongue-tear, lb.		
Warp	50	19
Filling	50	17
Water permeability (Hydrostatic resistance, psi)	300*	<1

* Burst point of fabric.

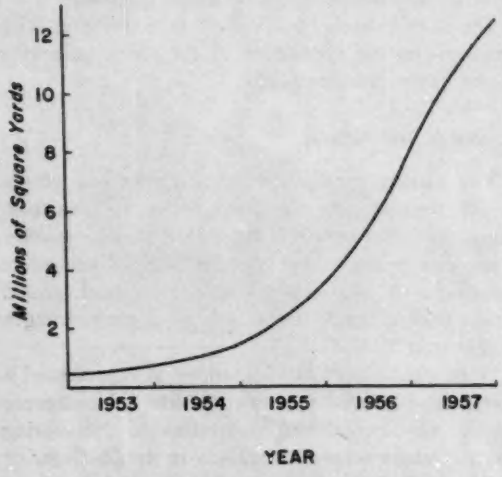


Fig. 6. Coated nylon fabric sales.

Other Uses

Other developments in existing markets, which warrant mention, include an improved rope construction intended to solve a problem of kinking which developed when certain types of rope of nylon or "Dacron" polyester fiber were repeatedly stretched. Here adaptation of a construction developed by the Navy has proved very effective.

Similarly, in fire hose, fish nets, sewing thread, textiles for the paper and laundry industries, plastic reinforcement, bearings, valve packing, gasketing, and filtration, synthetic fibers are gaining favor through the cooperative technical efforts of the fiber producer and his customers.

Future Developments

Looking into the future, we can anticipate continued development of new and improved fibers, tailored to meet the requirements of specific end uses, coupled with new end-use technology to assure maximum fiber utilization. The synthetics offer particularly challenging opportunities in this regard because of the wide array of physical and chemical property combinations which they offer, along with their adaptability. By adaptability is meant the ease with which special properties can be built into the fibers, such as shrinkability, stretchability, fusibility, dimensional stability, crimp and curl, and the like.

TABLE VI. Adhesion of Vinyl to Nylon

Fabric*	Adhesion, lb./in.†
Plastisol coated	
Typical commercial	12
Best commercial	21
Adhesive NVD	24
Laminated	
Open-mesh fabric	11
Adhesive NVD	21

* 5 oz. nylon base fabric except open-mesh item.
† Solvent test method.

When these features are viewed in combination with the versatility and cost–performance advantages offered by the new nonwoven structures, such as paper, bonded carded webs, and needled batts, it is easy to visualize use of synthetic fibers in a wide range of new industrial applications.

Recent Developments in Lofted Acetate Yarns for Apparel and Home Furnishing Fabrics[1]

R. E. Semmler

Eastman Chemical Products, Inc.[2]

R. F. Dyer, R. C. Forrester, and W. G. Faw

Tennessee Eastman Company[3]

Part I: Apparel Fabrics

IN THE continuous search for developing new and interesting fabrics, great potentials have been created by the use of textured or texturized yarns. These yarns are produced in different ways, but the most popular are those made from filament yarns. Our industry knows many modifications of textured effects from continuous filament yarns. Seldom has a development stirred the imagination as much as have textured yarns. While it is technically possible to texturize spun yarns, it is more logical to texturize filament yarns, and by this process to add certain properties by which spun yarns distinguish themselves, such as softer woolier hand, greater moisture absorption, more body comfort, and interesting styling potentialities, without having some of the disadvantages of spun yarn such as pilling and less uniformity.

Some of the texturized effects are produced in yarn by crimping, as in Ban-Lon, or by curling, as in Agilon. Stretch yarns as made under the Helanca system are considered by the trade as textured yarns, as may yarns from which the stretch has been removed, as in the Saaba method. However, only those yarns in which the textured effect has been obtained by the formation of crunoidal loops will be discussed; the topic will be further confined to cellulose acetate yarns. Eastman calls these yarns "lofted Estron" when spun from natural, and "lofted Chromspun" when spun from solution-dyed acetate.

Lofted Estron yarn is made by taking a continuous filament yarn and passing it through a lofting jet. In this lofting unit, air is employed to blow loops and entanglements into the filaments. During the lofting operation, the input and output speeds of the yarn are preferably accurately controlled at a ratio which will allow for an increase in denier caused by the loops which are blown into the filaments. Generally, the denier is increased 10–20% in the lofting process. This operation gives a yarn which has a much greater specific volume and larger diameter, is not quite as uniform, and has somewhat lower physical properties than the original continuous filament yarn from which it was made. Figure 1 shows the small loops in the individual filaments nonuniformly spaced along the strand of yarn. Only a portion of the filaments in any given length of yarn contains these small loops. Thus, the lofted yarn is similar to a novelty-type in which the straight or unlooped portions of filaments form the core and the looped or lofted filaments form the novelty effect. These loops in the filaments of the lofted yarns are an integral

[1] Presented at the 28th Annual Meeting of the Textile Research Institute, New York City, March 14, 1958.

[2] Subsidiary of Eastman Kodak Company, 260 Madison Avenue, New York 16, New York.

[3] Division of Eastman Kodak Company, Kingsport, Tennessee.

part of the yarn and will not pull out during normal textile processes through which the yarn is passed in the manufacture of a fabric.

Physical Properties of Lofted Yarns

In lofted yarns it is desirable to know the covering power of the yarn, which in turn affects the nature of the cloth in regard to such factors as hand, appearance, thickness, weight, and cover. An accurate measurement of the degree of lofting would make it possible to calculate the amount of yarn that could be wound on beams, bobbins, or cones, and to compare the bulk of various yarns. To meet these needs Tennessee Eastman Company has designed and built a tester to measure the bulk of yarns expressed in terms of specific volume. It consists of a steel wheel, as shown in Figure 2, mounted so that the yarn to be tested is wound under controlled tension to fill the wheel to the top of the flange. This provides a known volume of yarn which can be weighed. From the weight and volume, the specific volume can be calculated. Figure 3 is a schematic drawing of the bulk tester showing how the yarn is drawn from the supply package through a compensating tension device at a predetermined tension (usually 0.1 g./den.), then through a measuring tensometer and from there onto the bulk wheel. The yarn is cut off the bulk wheel and weighed accurately. By use of the volume of the wheel in cubic inches and the weight of the yarn, the specific volume is calculated by a simple formula as follows:

$$\text{cu. in./lb.} = \frac{\text{volume of wheel (cu. in.)}}{\text{weight of yarn (lb.)}}$$

Lofted yarns have a specific volume in the range of 70–100 cu. in./lb., while continuous filament yarns show a figure of 30–34 cu. in./lb. Figure 4 is a bar chart showing the comparative bulk of various Estron yarns. The increased bulk of lofted yarns means more coverage per pound and more cover per dollar.

With regard to other physical properties, the lofted yarns are about 38% lower in tensile strength than continuous filament yarns and about 28% lower in elongation. In spite of this reduction, strength and elongation are adequate for textile processing and fabric requirements within the range of yarn sizes normally used. Another outstanding physical property of lofted yarns is uniformity. While lofted yarns give a rough texture similar to staple spun yarns, they are actually more uniform

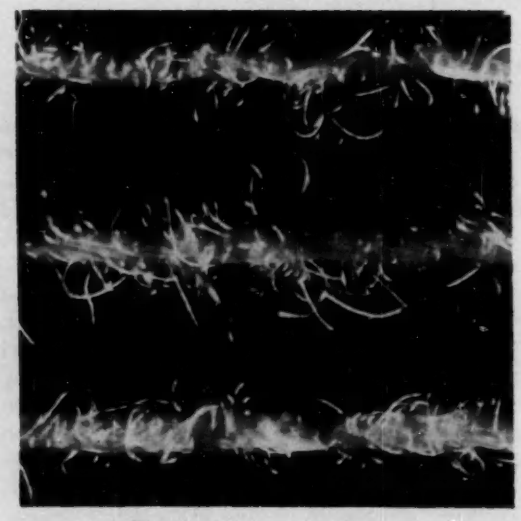


Fig. 1. 350-den. lofted Estron.

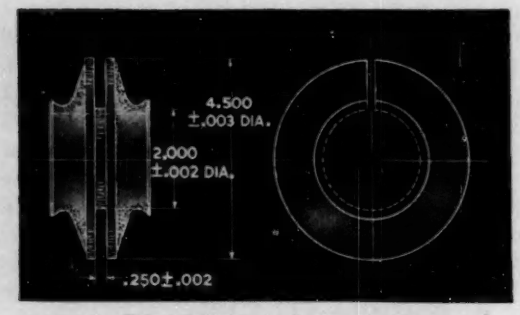


Fig. 2. Bulk wheel take-up roll.

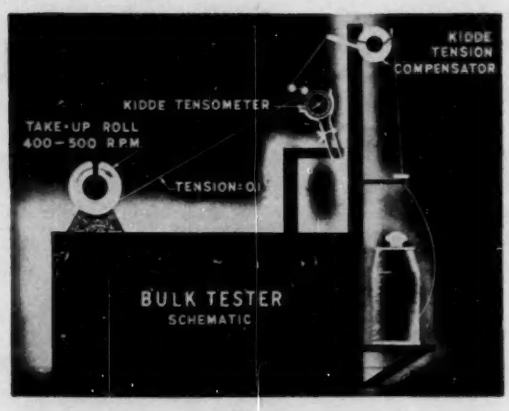


Fig. 3

TABLE I

Denier	Ends/dent	Finest reed recommended, dents/in.	Reed air space, in.	Yarn diameter, in./dent
230	1	60	.0087	.011
230	2	32	.0173	.022
350	1	54	.0095	.014
350	2	27	.021	.028
1080	1	28	.0207	.029
1080	2	14	.0444	.058
2200	1	19	.0326	.045
2200	2	10	.062	.090

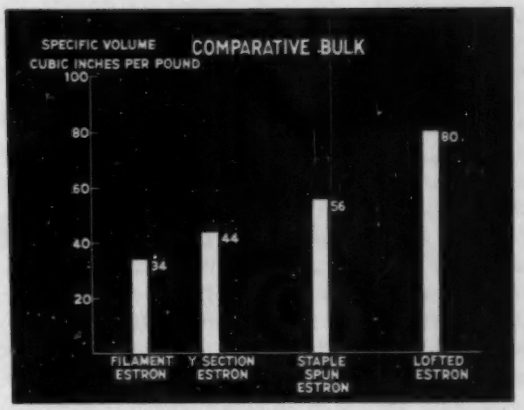


Fig. 4

than the staple yarns. Figure 5 shows this difference in uniformity in Uster charts run on three yarns of comparable size.

15/1 spun acetate—83% variation
350-den. lofted Estron—5% variation
300-den. Estron—less than 1% variation

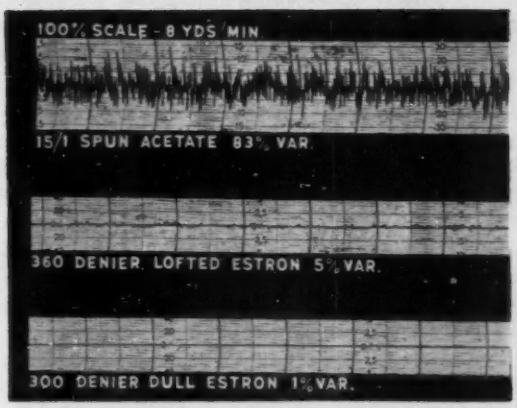


Fig. 5. Uster uniformity charts.

A distinction of lofted yarns is their special kind of luster. This is a silky, pearly luster not exactly duplicated in any other fiber, and it is this quality which is to some extent responsible for their popularity in sport shirtings, to which we shall refer later. Fabrics made with lofted yarns are free from fuzz and pilling. Although tactile properties of lofted yarns are influenced by variations in filament size and shape, twist, and other factors, generally speaking, fabrics woven from lofted yarns have a drier, more wool-like hand than similar fabrics woven from spun yarns. Lofted Chromspun yarns produce fabrics with great clarity of color; but if tweedy effects are desired for fall merchandise, colors may be subdued and varied. Interesting effects may be obtained by lofting several colors together without resorting to a second twisting operation. Noteworthy also are cone-over-cone effects or combinations of lofted yarns with other types of yarn.

Warping and Weaving of Lofted Yarns

As we have seen, the loop configuration of filaments affects the physical characteristics, and this is taken into consideration in handling lofted yarns for warping and weaving. Different processing equipment, however, is not required. In warping, either the cotton or silk system may be used with equally good results. Tensions are of greatest importance, and minimum tensions are preferred to be used. This will normally be approximately one-half the tension used for a filament yarn of the same denier. Lower tension and the bulkiness of lofted yarn produce beams of lower density, of course, than beams made from spun yarns or filament yarns. Reeds and combs used in warping, beaming, and slashing must have sufficient air space to accommodate the diameter of the yarn, bearing in mind that knots must pass freely. Sharp angles in the yarn path should be avoided to prevent excessive tension build-up and unnecessary abrasion of the yarn.

Lofted warp yarns may be woven without size. Fabrics woven from unsized warps may be finished with a minimum of wet processing, thereby helping to maintain the characteristic hand in the finished

goods. However, in more critical constructions sizing improves weaving efficiency. Therefore, many mills prefer to size lofted warps. Lofted yarns pick up much more size than normal filament yarns because of the filament loops; consequently, the amount of sizing material in the formula is reduced to 75 or 80% of that normally used. At the same time, it is desirable to increase the amount of oils or waxes used by about 10 or 15%. Drying temperatures should be as recommended for the specific size being used; however, speeds should be reduced, since lofted yarns pick up more solution. In some cases, it may be practical to increase drying temperatures slightly; however, care must be used not to glaze or bake the warp yarn. Slashing stretch is important and must be held to a minimum (2–4%). Low size box temperature is helpful in maintaining low slasher stretch.

In weaving lofted yarns the most common problem is opening a clean shed. Warp tension and harness timing are very important. Warp tension should be 5–7 points (Crompton & Knowles warp tensometer) higher than that normally used for filament warps. Harness timing should be early; the higher the sley, the earlier the timing. Using the proper reed also is important. The nature of the yarns is such that they do not slip easily, and coarse reeds are therefore to be avoided. Reeds which produce marks in the greige cloth will show little or no improvement after finishing. Reed wires break up the clinging of adjacent ends. The best rule is to use a fine reed, one end per dent, in preference to a coarse reed with more than one end per dent. However, air space should not be less than 70% of the yarn diameter. Knowing the specific volume and denier of the lofted yarns, our Textile Development Laboratory in Kingsport determines the yarn diameter by the following formula:

$$\text{yarn diameter} = 2\sqrt{\frac{\text{denier} \times \text{specific volume (cu. in./lb.)}}{16 \times 10^7 \times \pi}}$$

According to this formula, a 350-den. lofted yarn having a specific volume of 70 cu. in./lb. would have a diameter of .014 in., and no finer reed than 54 dents per inch should be used. Reed air space for this reed, according to the tables published by Steel Heddle Company, is 0.0095, a fraction more than 70% of the diameter. In our Kingsport experimental weaving unit, we use Table I as a guide in selecting the reed to be used when weaving lofted yarns.

Lofted filling yarns may be wound on any type of filling winder. Tension should never be higher than necessary for good weaving and should be 5–10 g. lower than for a regular filament yarn of the same denier. With a No. 5 or No. 7 wind on the Abbott or No. 90 Universal quiller, the preferred tensions are as follows:

230 den. 30–35 g.
350 den. 40–45 g.
1080 den. 70–80 g.

Dyeing and Finishing of Lofted Fabrics

A great number of fabrics containing lofted yarns are used in the off-loom state without any finishing whatsoever. This is done in order to retain the original hand of the lofted yarn and also for economy. However, we prefer a light scouring and framing to remove the size and to obtain complete relaxation of warp and filling, thus avoiding any possibility of shrinkage. Although scouring changes the tactile properties of the finished fabrics, very often resulting in a softer hand, the spun-like character of the goods may be retained. It is also possible to adjust the hand as desired by the addition of resinous treatments. In case of fabrics composed of lofted yarn in both warp and filling, it is advisable not to do any slashing of the warp if the wool-like nature of the cloth is to be preserved. If slashing is used and scouring is necessary, either a firm finish or a "dry finish" may be obtained. The finishing process may involve mechanical manipulation of loom-state goods or the application of resins or water repellent finishes to produce the particular handle desired by the converter.

Fabrics with lofted yarns are well suited for all printing processes. The printing may be done with either loom-finished or processed goods. Piece dyeing of fabrics containing lofted yarns offers some difficulties. If the dyeing is done on the jig, the cloth loses the character attributed to fabrics made with lofted yarns; if on the box, rope marks are in evidence. One way to overcome this situation is by fabric construction. Combining the lofted yarn with another yarn promotes some shrinking-in and provides a scaffold to carry the lofted yarn through the folding and creasing manipulations during the dyeing operation. In Europe, no difficulties are experienced with piece dyeing of fabrics containing lofted

yarns. There is no objection there to dyeing on the star reel, whereas in the United States this method is not considered economically feasible. Therefore, at the present time we are somewhat limited in the use of lofted yarns for piece dyeing. Eastman is continuing research in this field.

Lofted Fabrics

As has been pointed out, the potentials of creating new effects in fabrics with lofted yarns are enormous. This holds true for apparel as well as for drapery, carpet, and upholstery fabrics.

Part II: Lofted Carpet Yarns

IN THE early 1950's it was recognized that the combination of the rapidly developing tufting process for producing carpets, solution-dyed acetate, and the lofting process held considerable potential for the development of 100% acetate carpets with attractive style features and good performance at a moderate price. Tennessee Eastman, therefore, proceeded with the development of a lofted acetate yarn tailored to the needs of the carpet trade; in 1956, carpets made from Eastman's lofted Chromspun yarn were introduced in the retail market. Since that time several mills have worked with lofted acetate yarns in both tufted and woven carpets; large numbers of consumers have installed these carpets. This paper reviews the characteristics of lofted acetate yarn which relate to its performance in the carpet mill in producing attractively styled carpets and compares the results of laboratory performance tests to actual consumer experiences.

Lofted Chromspun yarn is continuously spun from pigmented dope under closely controlled conditions which assure a high degree of color uniformity to the carpet industry. A carpet mill can thus establish a color with assurance that there will be a minimum of variation in yarn color. The inch-to-inch and yard-to-yard denier uniformity of lofted yarn is excellent. Figure 6, which illustrates this uniformity, shows that 3-ply lofted acetate has a denier variation in the order of ± 5%, whereas conventional 3-ply spun carpet yarns will vary more than ± 50%. This is of considerable significance for two reasons: first, the yarn is free from thick spots which may cause breaks on the tufting machine; second, in plied yarns the uniform denier promotes twist uniformity. In lofted filament yarns there are no thick spots in the yarn to cause the twist to run back to thin spots in the ply. In tweed yarns this reduces variations in the color effect. Texture variations in the carpet resulting from uneven yarn are also minimized. On the other hand, while denier and volume uniformity of lofted carpet yarn promote mill efficiency and make possible new styling approaches, it also imposes the need for care in controlling the yarn size and in establishing the proper twist in plied yarns. A third advantage, and perhaps the most important, is the high covering power and bulk of lofted acetate as compared to staple yarn.

Obviously, price and style are two factors on which a customer largely bases the decision to buy; another factor is performance. Here the reputation of the carpet retailer is the paramount factor in leading the consumer to the selection of one carpet in

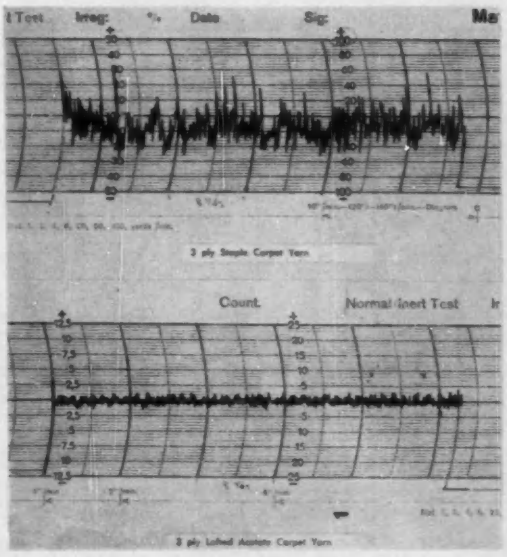


Fig. 6

preference to another. To provide the consumer with guidance and facts required to assure satisfaction, the carpet retailer must be provided with an accurate picture of the performance of the carpet fibers and styles which he is selling. The burden of collecting this information and disseminating it falls on the fiber producer and the carpet mill.

The Textile Development Laboratories of Tennessee Eastman Company have studied the problem of predicting carpet performance very carefully ever since the development of lofted acetate carpet yarn was begun. The problems of obtaining test data quickly and weighing the numerous factors of soiling, cleanability, stain resistance, abrasion resistance, resistance to matting, retention of texture, hand, color, style, and price to achieve a well balanced yarn can not be easily solved. It matters little how outstanding a carpet may be in one or more of these factors if it is too deficient in one or more of the other factors.

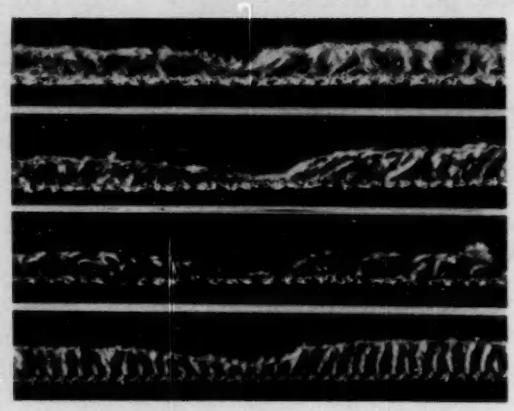


Fig. 7. Stairway abrasion test. Top to bottom: wool loop pile, lofted acetate loop pile, viscose loop pile, lofted acetate saxony cut pile.

In evaluating lofted acetate as a carpet yarn, a wide and complete range of testing is performed in Tennessee Eastman's laboratories, as well as in homes in the area and in laboratories associated with the carpet mills and carpet cleaners' organizations. This testing is essential because with natural fibers one must make the best of what nature produces, while man-made fiber can be varied at many steps in the manufacturing process to adjust the yarn properties and thus to achieve a balanced combination of properties in a desired price class.

In evaluating lofted acetate a great deal of weight has been placed on the results of actual use tests of carpet samples. Accelerated laboratory abrasion, soiling, and resilience tests will often produce valid data on a given fiber composition and carpet style, but very misleading results can be obtained in comparing different fibers and carpet styles in woven and tufted structures. Even in actual use testing,

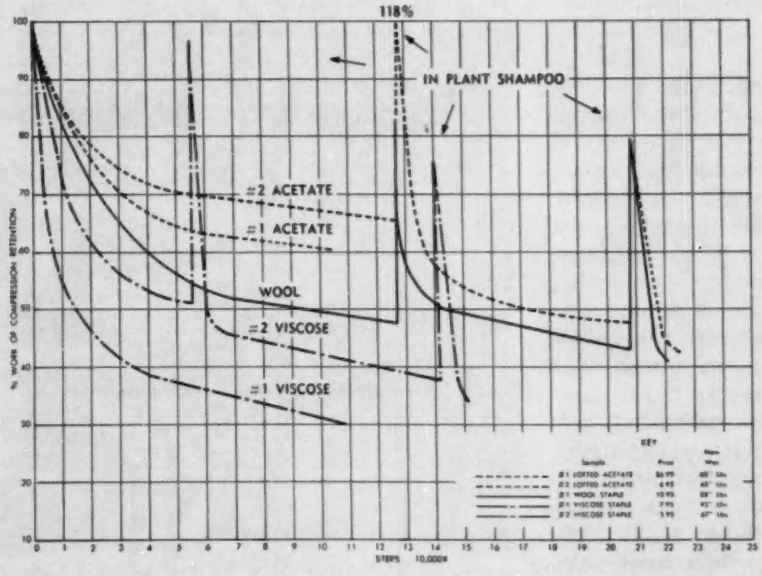


Fig. 8

caution must be exercised to avoid drawing broad conclusions from only one type of use test. A carpet which may perform rather well in resisting abrasion on a stair test may fail very rapidly on a straight-away walking test because of the effects of heavy traffic on the texture, soiling, and resilience.

Abrasion testing on lofted acetate is performed in a number of manufacturing and office areas in the Kingsport plant of Tennessee Eastman Company. Carpet samples are attached to removable sheet metal treads with a uniform edge radius of 0.75 in. The treads are interchanged so that each carpet is exposed to each location at least once in a test cycle. No padding is used. Traffic is very heavy, about 2000–3000 walkovers per day in both the down and up directions. The traffic is about 70–80% separated in the up and down directions, which affords a comparison of carpets subjected predominately to edge wear on the down flight and a scuffing abrasion on the up flight tread. Careful observation of the test is made frequently. On loop-pile carpets two points of wear are recorded as "loops completely broken" and "one row of stitches worn to the backing." More weight is placed on the latter point, as most staple yarns wear out by loss of fibers in the yarn, so that the loops gradually thin down and suddenly disappear. Cut-pile carpets are evaluated by loss of pile height and the steps required to wear out one row of tufts on the stair edge. On the up flight the tread wear is evaluated subjectively, as no definite end points of wear are encountered in the normal test. After the test is completed, the carpets are sectioned and one-half is cleaned by a rotary shampoo; photographs of the cross section of the carpet are made. Figure 7 shows the results of a typical wear test run for an equal number of steps on all carpets. In the photographs the matting of the pile and the width of the abraded area serve as a measure of the resistance to abrasion and matting. In the figure a $6.95 lofted acetate, a $6.95 staple viscose, and a $10.95 wool loop-pile, all of about equal construction, are compared. This test represents a typical competitive market-value test. In evaluating manufacturing variables on a given fiber, equal constructions are used without regard to price. The reason for this can readily be seen in the fourth carpet, which is a twist-set, cut pile, lofted acetate carpet that showed excellent abrasion resistance.

As an adjunct to the stairway testing, which is primarily for abrasion, long-term floor tests are conducted in areas where there is heavy traffic in a straight path, with no turning off. Carpets again are rotated regularly to level out local wear conditions.

In floor testing, the evaluation of soiling in areas of both greasy and dry soil and the cleanability are observed closely. In addition, loss of thickness, changes in initial plushness, or hand and texture changes are closely observed and measured. Thickness loss or matting and plushness or work of compression are measured on the new carpet and at intervals thereafter. It is felt that any departures from the original thickness, texture, plushness, and color are most undesirable to the consumer, since carpeting was purchased on the basis of its original appearance in the store. The usual test is run for 20,000–30,000 steps, although some tests are run to several hundred thousand steps and include on-floor cleaning at intervals. Figures 8 and 9 show results of a typical long-term work of compression and thickness retention test on comparably constructed and styled viscose, acetate, and wool carpets that were shampooed at intervals during the test. It will be noted that acetate approached wool rather closely in thickness and work of compression retention, although it was somewhat lower in initial work of compression. A low initial work of compression, which means a hard finish with a firm hand, is a desirable characteristic in loop-pile carpets, judging by consumer reactions. Obviously, from a service point of view, good retention of initial thickness and work of compression are highly desirable. The viscose carpet had a high initial work of compression but changed rapidly in use because of a severe loss of thickness and matting of the fibers. It is interesting to note the relatively short-lived effect of shampooing operations on the carpets. It might also be noted that these carpets, which were of about 31-oz. weight, would have been considerably upgraded by the use of additional yarn. For example, a sample lofted acetate carpet containing about 45 oz. of yarn of equal pile height would have shown considerably less loss in thickness or change in plushness during the test.

A very effective manner of evaluating the effect of changes in manufacturing variables on a given carpet is the tufting of narrow bands of the experimental yarns in rotation with a control yarn. This method is also effective for comparing abrasion, thickness, and work of compression performance.

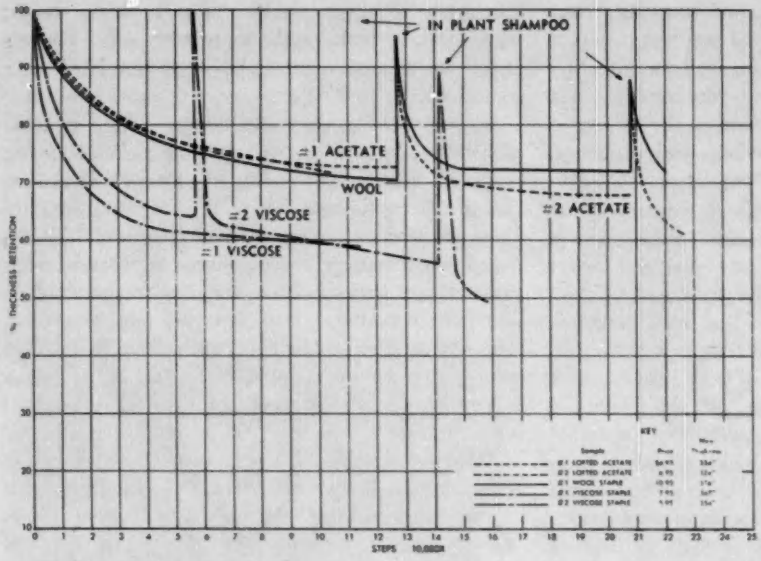


Fig. 9

Fig. 10

In many homes today the combination of pets, children, and TV dinners makes spot and stain removal a very important factor in carpet performance. Figure 10 shows the excellent results of stain removal tests made on lofted acetate carpeting.

The foregoing summary of the development and testing of lofted acetate carpets would be incomplete without a few comments on the consumers' opinions after having these carpets in their homes for over a year. In a survey of a group of early buyers of lofted Chromspun carpet conducted recently, it was found that the carpets had been bought mainly by small home owners of modest income as their first carpet. There were, however, several installations in dens, TV rooms, and bedrooms of higher-income homes where an expensive carpet was usually installed in the living room. Ninety-four percent expressed satisfaction and said they would buy a lofted Chromspun carpet again under similar circumstances, although several hoped to upgrade to a higher quality, probably wool or wool-synthetic blend, if they could afford it. Seventy-five percent commented on the excellent spot and stain removal characteristics of their carpet. In making their purchases, style, price, and the reputation of the retailer were the prime factors and were given about equal weight. The carpet cleaning organization associated with the store participating in the survey was pleased with the cleanability and appearance of the carpets that were cleaned, commenting that some of the man-made-fiber carpets were very difficult to clean, especially in light colors.

In summary, on the basis of mill, laboratory, and consumer experience, lofted acetate has attained a definite place in the carpet field by offering wide styling possibilities; good retention of color, texture, thickness and hand; excellent stain and spot removal; good soil resistance and cleanability; and wear resistance, all in a price range which puts carpeting of the home within the means of the family of average income.

Chemical Modification of Cotton: Progress and Current Status[1]

C. H. Fisher and F. S. Perkerson

Southern Regional Research Laboratory,[2] New Orleans 19, Louisiana

BECAUSE of vast research programs and dramatic successes in the field of man-made fibers, it has been easy to overlook the fact that research on cotton also has enjoyed spectacular success. More progress has been made in cotton research in the last decade or so than in the past several centuries. Taking chemical modification as an example, there has been unprecedented progress in both research and manufacturing.

The fact that recent years have witnessed real progress in the chemical modification of cotton is worthy of note because this is in sharp contrast with the previous history of the textile industry. For centuries the textile industry was essentially mechanical in nature. Except for bleaching, printing, and dyeing, chemical processes played little part in the centuries-old manufacture of cotton textile products. Even when chemistry was applied actively to the development of new textile products, it was applied primarily to synthetic fibers.

Because of the success of chemistry in recent years in transforming cotton into valuable new products, many new cotton products of diverse nature are now commercially available. One of these—wrinkle resistant and "minimum care" products—is manufactured on a scale greater than the total manufacture of the hydrophobic man-made fibers [64].

In the present paper, the term "chemical modification" will include any chemical treatment of cotton that will cause durable, substantial changes in properties. This paper will not discuss the older conventional processes such as scouring, bleaching, mercerizing, and dyeing.

[1] Presented at the 28th Annual Meeting of the Textile Research Institute, New York City, March 14, 1958.

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

20th Century: Chemically Modified Cottons Are Born

The successful use of chemicals to impart durable, significant changes to cotton is a development of this century. This development represents the union of two industrial giants—centuries-old cotton and the youthful, vigorous chemical industry.

The desire to have dye resist yarns apparently dominated the early work. At the beginning of the century Cross and Schneider prepared dye resist yarns by acetylating [12] and nitrating [58] cotton yarns.

Three dye resist products from cotton were made commercially [77] in the 1920's: the benzoate (reserve cotton), toluenesulfonate (immunized cotton), and acetate (passive cotton).

Cotton textile products having amine groups and increased receptivity to some dyes were made by causing the fibrous toluenesulfonate of cellulose to react with ammonia or amines [33, 34].

Acetylated cotton (Cotopa 30),[3] based on patents of A. Rheiner of Sandoz A. G., has been manufactured in England from 1928 to the present [22, 38, 55, 56].

In 1928 patents issued to Tootal Broadhurst Lee in England showed that some degree of wrinkle resistance and dimensional stability could be imparted to rayon and cotton by the application of urea-formaldehyde resins [22, 37].

Soluble cotton gauze, made by oxidation with nitrogen dioxide, has been used in the U. S. for some years as a surgical dressing [73]. Nitrated cotton yarns have been manufactured and used because of their property of becoming soluble under some conditions in alkaline solutions [37].

High-style cottons have been manufactured both

[3] The mention of organizations and commercial products should not be construed as an endorsement of these over others not mentioned.

in the U. S. and abroad and finished by parchmentizing, embossing, pleating, and applying high polymers [30].

Hydroxyethylated cotton was made and studied intensively about 1940. This product has a crisp hand, linen to parchmentized appearance, and enhanced reactivity and dyeability [36].

Water repellent cottons, made by treating cotton with stearamidomethylpyridinium chloride, octadecylethyleneurea, ketene dimers, alkyl pyridinium salts, or certain betaines, methylolamides, and methylolureas [10, 37, 59] have been available.

This brief review takes us to the second half of the 20th century, which, even in the brief period of eight or nine years, has witnessed further significant progress by chemically modified cottons.

Current Status of Chemically Modified Cottons

Since 1950 advances in the science and manufacture of chemically modified cottons have been impressive in at least three respects—the number and total volume of these products and the improved understanding of the problems involved in making them.

Partially acetylated cotton, called "Izopa," is now manufactured in Hungary [78, 79]. Presumably Izopa is similar in properties to Cotopa 30 made in England and partially acetylated (PA) cotton made in the United States.

Cotton fabrics treated commercially with high nitrile-rubber latices have been reported [1] to have certain durable properties, e.g., improved abrasion resistance. Additional information on some of the commercially available chemically modified cottons is given in Tables I and II.

The estimated cost of applying certain chemical treatments to cotton is given in Table III.

The total cost of the products is given in Table IV. While these cost data are preliminary and approximate, they indicate that some chemically modified cottons, when made under favorable conditions, are attractive from the standpoint of cost.

Buras [6] and Compton [9] have reported that the costs of acetylating and cyanoethylating cotton are 14¢ and 13–16¢ per pound, respectively.

TABLE I. Manufacture of Chemically Modified Cottons

Designation	Initiated	No. of manufacturers	Available as	Remarks*
Wrinkle resistant, wash-wear	1955†	Many	Fabric garments	
Partially acetylated:				
Cotopa 30	1927	1	Yarns	Made in England
			Fabrics	
PA cotton	1953	1	Fiber‡	
		1	Fabrics	
Fully acetylated:				
Cotopa 60	1936	1	Yarns	Made in England
			Fabrics	
FA cotton	1957	1	Fiber‡	
Carboxymethyl (CM) cotton	1957		Yarns‡	
		1	Fabrics‡	
Alkali-soluble	1956	1	Fabric	Made by oxidation of etherified cotton
THPC-cotton**	1956	Several	Fabric	Product made in England called "Proban"
BAP-cotton††	1957			
Tobacco shade cloth (weather resistant)	1953	2	Fabric	Made by treatment with lead chromate

* Data pertain to U. S. unless otherwise noted.

† The year when the manufacture of wrinkle resistant and wash-wear cottons became significant; total volume of resin-treated cotton fabrics, about 1.4 billion yards in 1956.

‡ Commission basis.

** Flame resistant cotton made with tetrakis(hydroxymethyl)phosphonium chloride.

†† Flame resistant cotton made with the bromoform adduct of allyl phosphate.

Because fully acetylated (FA) cotton listed in Tables I–IV has essentially the chemical structure of cellulose triacetate, it is related to the fibers made by extruding solutions of cellulose triacetate. Some of the differences are: fiber dimensions and shape; FA cotton [7] is insoluble, whereas the extruded fiber is soluble in some solvents; and FA cotton has higher molecular weight than the extruded product. FA cotton resembles the extruded triacetate in having certain thermoplastic properties under some conditions. That is, it can be durably calendered, embossed, and pleated.

Chemically Modified Cottons Investigated in Pilot Plant

Aminized (AM) cotton, made by treating cotton with 2-aminoethylsulfuric acid in the presence of alkali, has been studied extensively [46]. Because it has primary amine groups (Cell-$OCH_2CH_2NH_2$), AM cotton has ion-exchange properties and increased chemical reactivity and affinity for some dyes.

Following the dissemination of information on cyanoethylated cotton by the Institute of Textile Technology [9], several organizations have made this product in relatively large quantities. It has been extensively evaluated for the many end uses indicated by its improved resistance to rot and heat and enhanced affinity for some dyes [32].

Extremely durable flame resistant cotton products have been made on pilot plant [45] and semicommercial scales by treatment with a mixture of equimolar portions of APO (triethylene phosphoramide) and THPC [tetrakis(hydroxymethyl)phosphonium chloride], both commercially available chemicals. The outstanding features of this treatment are its effectiveness with relatively small amounts of material added and its durability to repeated severe launderings. More recently it has been found that APO can be applied with certain catalysts, and without the THPC, to impart excellent wrinkle resistance [66].

Progress in Developing Improved Wash-Wear Cotton Garments

Whether made from cotton [11, 50], synthetics, or blends, the growth and success of wash-wear products, introduced in 1952, has been remarkable [2, 64]. The scales curve has gone up steeply each year. It has been estimated that 1,700,000 men's and boys' wash-wear summer suits were sold in 1957, that the approximate retail value of wash-wear garments

TABLE II. Principal Properties and Uses of Chemically Modified Cottons

Modified cotton	Principal properties	Principal uses	Potential uses
Wrinkle resistant, wash-wear	Enhanced resilience, elastic recovery, and rot resistance	Wrinkle resistant wearing apparel, wash-wear garments, household goods	
Water repellent	Water shedding	Rain-wear garments	
Acetylated cotton	Greatly improved resistance to rot and heat—improved insulating properties (electrical)	Ironing board covers, dye resist yarns, electrical insulation	Paper makers dryer felt
Vat dyed, acetylated cotton	Improved weathering resistance		Irrigation pipe and dams—outdoor uses such as awnings, tarps, etc., and sewing threads for such products
Carboxymethylated (CM) cotton	Increased affinity for water and some dyes—increased chemical reactivity—ion-exchange properties		Production of alkali soluble cotton—base fabric for resin treatment without catalyst
Alkali soluble	Soluble in moderately alkaline solutions	Scaffolding textile products	
Soluble gauze	Soluble in body fluids	Surgical dressing	
Flame resistant cottons	Resistant to burning—rot and wrinkle resistance	Wearing apparel and household goods	Tents, awnings, tarps
Lead chromate treated	Improved weather resistance	Shade cloth for tobacco	

reached $350 million in 1957, and that 1.4 billion yards of crease resistant and wash-wear cotton fabrics were produced in 1956 at a cost (for the treatment) of about 3¢ to 5¢ per yard [64].

Early work [13, 18, 21, 22] by the Southern Laboratory in this general field was concerned primarily with the colloidal structure of cotton cellulose and pretreatments (decrystallization with amines; mercerization under various conditions; and the attachment of carboxymethyl, aminoethyl, hydroxyethyl, and other groups) that might make the cotton more suitable for treatment with wash-wear chemicals. Major objectives of the earlier work were to provide fundamental information and pretreated cot-

TABLE III. Estimated Costs of Treating Cotton to Make Chemically Modified Cottons *

Chemically modified cotton	Method	Cents		Assumed annual production (millions)	Remarks
		Lb.	Yd.		
Wash-wear trousers	Batch		23†	0.875	
PA cotton yarn	Continuous	14.2	—	61.5 lb.	15% acetyl; 90% chemical recovery
PA fabric, 60 in. wide 8 oz./lin. yd.	Continuous	16.8	9.6	12.1 yd.	15% acetyl; 48 × 48 sheeting; 90% recovery; 9.2 oz./lin. yd. finished weight
FA yarn	Batch	41.0	—	6.5 lb.	40.6% acetyl; 90% chemical recovery
CM fabric, 60 in. wide 6.15 oz./lin. yd.	Continuous	9.15	3.9	25.2 yd.	80 square print cloth; D.S. 0.095; 6.82 oz./lin. yd. finished weight
THPC fabric, 60 in. wide 13 oz./lin. yd.	Continuous	15.0	14.2	60.5 yd.	8 oz. O.D. twill; 16.6% add-on, 15.1 oz./lin. yd. finished weight
AM fabric, 60 in. wide 6.15 oz./lin. yd.	Continuous	29.1	11.5	5.04 yd.	80 square print cloth; 0.7% N; 6.32 oz./lin. yd. finished weight
HE fabric,‡ 60 in. wide 6.15 oz./lin. yd.	Semi-continuous	16.3	7.4	25.2	80 square print cloth; D.S. 0.6; 14.3% add-on, 7.26 oz./lin. yd. finished weight

* Calculated for favorable conditions; costs for isolated runs would be higher.
† Cost per garment.
‡ Hydroxyethylated, using ethylene oxide.

TABLE IV. Total Cost per Pound of Chemically Modified Cotton

Chemically modified cotton*	Cost of treatment, ¢/lb. product	Assumed annual production, millions of pounds	Total cost, /lb.	Selling price, /lb.
PA yarn; 15% acetyl (continuous)	14.2	61.5	69.4	$1.04†
PA yarn; 15% acetyl (batch)	19.1	4.8	74.3	1.11†
FA yarn; 40.6% acetyl	41	6.5	81.6	1.22†
Nylon				1.20‡
Dacron**				1.50‡
Saran				1.32‡

* Yarn, 8/5 carded, 1-in. middling.
† Cost plus 50%.
‡ Minimum.
** Du Pont trademark.

tons that would yield wrinkle resistant garments of improved properties, particularly tear strength.

During the last 18 months, wash-wear problems have been investigated in the Southern Laboratory on a larger scale [49–51] in cooperation with the National Cotton Council and several industrial organizations [24, 25].

One limitation of existing commercial methods is that desired pleats or creases cannot be placed satisfactorily in garments made from fabrics that have been previously resin-treated to confer wash-wear properties. The three principal methods now being studied for obtaining durable creases in cotton garments are:

1. Application of resins to finished garments followed by pressing and curing.

2. Application and curing of resins on piece goods followed by (a) manufacture of garments, (b) application of catalyst to areas where creases are desired to reactivate the resins, and finally (c) creasing and recuring.

3. Application of resins to piece goods and drying but not curing, followed by manufacture into garments, then creasing and curing.

Excellent cotton garments worthy of the expression "wash-wear" have been produced at the Southern Laboratory by applying dimethylol ethyleneurea and certain other agents to the entire garment. The products have durable creases and complete launderability in home-type washers and tumble driers. Chemical costs were low, averaging 2–4¢ for some garments.

Work at the National Institute of Drycleaning [6] has shown that it is feasible to use conventional commercial equipment in applying the improved formulations to cotton garments as described above [24, 25].

Recent wash-wear developments from research done at, or supported by, the Southern Laboratory include: new cross-linking agents such as APO (triethylene phosphoramide) and carbonyl bis-aziridine (made by treating ethylenimine with phosgene), that have certain advantages, e.g., freedom from chlorine retention or enhanced resistance to burning; use of N-ethylenestearamide or related long-chain reagents to attach internal softening or plasticizing groups to the cellulose or the resin with considerable improvement in tear strength and abrasion resistance; and development at the Fabrics Research Laboratory [6] of fabric constructions [31, 67] that might be attractive for wash-wear purposes because they have relatively high tear strength after resin treatment.

[6] Research done under contract for Agricultural Research Service, U. S. Department of Agriculture.

Additional Progress in Developing Chemically Modified Cottons

New cotton fabrics that shed both oil and water have been developed, utilizing commercially available materials [43, 62]. Two treatments—both based on fluorochemicals—give these results. In one treatment, cotton fabric is passed through a colorless latex of a fluoro-rubber and dried. In the other treatment, a chromium complex of a perfluoro-organic acid is padded onto the fabric, then air or oven dried. White fabric turns a very pale green with the latter treatment, but the tint is not enough to affect medium or heavily dyed fabric.

Oil drops which readily penetrate untreated cotton fabrics will not normally penetrate the treated fabric —even after two weeks of contact. Water drops remain on the treated cloth until they evaporate. Fabrics treated with the chromium complex are resistant to soiling.

Cyanoethylation and certain other etherification reactions of cotton can be conducted more rapidly and with less undesirable side reactions by use of certain salts that increase the water solubility of the organic reagent or swell the cellulose [4]. For cyanoethylation the yield obtained under conditions comparable to pilot plant practice was tripled.

Hydrotropic substances such as sodium xylene sulfonate have been used to prepare the benzyl and 2,4-dinitrophenyl ethers of cellulose under conditions maintaining the textile properties of the fiber [66].

Low-cost and uniformly coated cotton products having excellent resistance to rot and good resistance to chemical attack and abrasion have been prepared by polymerization of acrylonitrile vapors within and upon the fibers of cotton yarns and fabrics [23, 29]. Breaking strengths were materially increased, particularly when the polymer was formed on yarn and fabric held under tension.

The kinetics of the fibrous acetylation [61] and benzoylation [3] of cotton have been studied. The rate of acetylation increases in the order: cotton, ramie, hemp, and flax [15].

Takagi has made fully acetylated cellulose fibers by treatment of the fibers with vapors of acetic anhydride [69].

Recent experiments have shown that some chemically modified cottons esterified or etherified to suit-

ably high degrees of substitution (more than about 25% acetyl for acetylated cotton) have thermoplastic properties [66]. Such acetylated cottons can be pleated, embossed, and glazed and then made durable to more than five launderings by pressure steaming. Heat stressing of PA and FA cottons caused greatly reduced growth after cyclic loading and increased elastic modulus without markedly affecting breaking strength [66]. Esters of cellulose with acids other than acetic acid exhibit similar properties, which suggests that many thermoplastic cottons, having attractive possibilities, are possible.

Many esters of cotton cellulose have been made by the use of various organic acids and trifluoroacetic anhydride [28]. The results of this study indicate that this comprises a useful, versatile method for making many new fibrous cellulose esters.

It has been shown in a preliminary investigation [19] that a number of activated olefinic compounds (acrylamide, acrylic acid, maleic acid, etc.) can be made to react with cotton cellulose, forming fibrous cellulose ethers.

Pacsu and coworkers [41, 60] at the Textile Research Institute have studied a new approach to preparing flame resistant cottons. The process involves the preparation of mesyl or tosyl derivatives of cotton cellulose followed by treatment with potassium bromide or sodium iodide to partially replace the mesyloxy or tosyloxy groups with the halogen. A similar technique has been used by Klein and Snowden [35] to replace the mesyloxy or tosyloxy groups with halogen, amines [33, 34, 76], phthalimide, thiophenols, saccharine, substituted phosphoric acids, and nitropropane. In earlier work, Reid and his coworkers [47, 48] reported that replacement of hydroxyl groups with chlorine accompanied phosphorylation with phosphorus oxychloride. Iodine has been introduced also by treating fibrous cellulose phosphate with sodium iodide [48].

Fetscher [17], Reid [53], and others [36, 39, 46, 65] have modified cotton durably by preparing graft polymers of the cellulose. Fetscher made allyl and other unsaturated derivatives of the cellulose and then—through treatment with vinyl-type monomers—attached polymer chains to the cellulose.

One of the barriers to making new and useful cotton products by chemical modification is the excessive stiffness and other undesirable properties resulting from some chemical treatments. It has been found that cross-linking the cellulose prior to chemical modification prevents or minimizes the undesirable effects, thus permitting high degrees of chemical modification [66].

Guthrie [27], Vickerstaff [75], and others [8, 42] have described methods for attaching dye molecules directly to cotton cellulose.

Esteve, Wright, and Mack [16] at Texas Woman's University [4] have applied about 100 inorganic compounds to cotton to effect durable improvements in textile usefulness. The results indicate that cobaltous hydroxide, and particularly cobaltous metaborate, can increase weather stability 3- to 6-fold and rot resistance up to 10-fold. The metaborate also conferred water repellency. Magnesium and aluminum hydroxides, colorless and inexpensive, imparted weather and flame resistance.

Lead chromate is well known for its favorable preservative qualities for tobacco shade cloth. It was found by Esteve, Wright, and Mack [16] that lead hydroxide also has valuable properties; it imparted water repellency, heat stability, and some flame resistance.

Methods for imparting durable fragrance [44] to fabrics and the ability to decrease body odors [57] have been described.

Work in several organizations, including the School of Textiles, North Carolina State College, Massachusetts Institute of Technology,[4] and the Southern Laboratory, has shown that ionizing radiations have a degrading effect on cellulose [20, 71]. It has been indicated that significant changes in cellulose structure (creation of carbonyl and carboxyl groups) can be effected before the molecular weight drops low enough to destroy textile usefulness [5]. Preliminary work [66] indicates also that certain chemicals applied to cotton can be caused to react or polymerize by irradiation before the cellulose is seriously damaged. Much additional effort will be required to evaluate adequately the potentialities afforded in cotton research by high energy radiations. The acquisition of cobalt-60 facilities at the Southern Laboratory will accelerate such studies.

Preliminary work has indicated that it is advantageous in some instances to blend untreated cotton with chemically modified cottons. For example, a blend of 60% PA cotton with 40% untreated cotton has the advantages (compared with 100% PA cotton) of lower cost, enhanced processing ease, and improved breaking strength and abrasion resistance. In addition, the blend retained much of the high heat resistance characteristic of PA cotton alone.

A preliminary study of blends of THPC cotton

(flame resistant) with untreated cotton has indicated that this approach has certain advantages in making flame resistant yarns and fabrics. It has been observed that cotton fibers treated with a mixture of APO and THPC can be processed readily [66].

Some Problems Involved in Developing Chemically Modified Cottons

The foregoing account, which has emphasized advances, should not convey the erroneous impression that scientists have acquired most of the information needed to develop, evaluate, and use chemically modified cottons efficiently. Indeed, the problem of developing and manufacturing such products can be as complex and difficult as that involved in developing new synthetic fibers. The variables and possibilities involved in studying chemically modified cottons are numerous. Even for PA cottons, which have apparently received more attention than other chemically modified cottons, many important variables have received insufficient attention.

Variety of cotton. One investigation [70] indicates that the effect of variety on cellulose reactivity to acetylation is related to maturity and Micronaire fineness.

Morphological properties. Information on this variable (closely related to the variety) apparently is limited to the observation that fine cottons (low Micronaire values) acetylate, cyanoethylate, and carboxymethylate more readily than cottons with high Micronaire values [26, 52, 54, 70]. Immature fibers acetylate more readily than mature fibers [70]. Presumably fine cottons and the fine or thin portions of the fiber are generally more reactive chemically than thick fibers or the thick parts of the fiber [72].

Effect of trace materials. Little is known about the effect of waxes, salts, organic acids, pectin, proteins, etc. that occur naturally on and in cotton fibers. Some of these are removed during pretreatments. It has been observed that material superficially resembling cellulose acetate is in the acetylation mixture resulting from making PA cotton [7, 66].

Pretreatments to purify or activate the cotton cellulose. This field has received considerable, but inadequate, effort for some types of chemical modification [14, 74].

Tightness of yarns and fabrics. Chemical reactions are retarded for tight or closely packed fibers, yarns, and fabrics.

Tension of yarn and fabric. It has been observed in a number of instances that tension leads to products having higher tensile strength and lower elongation.

Reaction conditions and catalysts. Because considerable information has been obtained in this area, it is possible to generalize about some aspects of reaction conditions for some reactions.

Reactions that occur in low swelling media yield products with the substituents located primarily in the amorphous regions (for relatively low degrees of substitution). On the other hand, under conditions that cause considerable cellulose swelling the substituents are usually distributed more uniformly throughout the fiber.

Another generalization is that the reaction medium must have limited capacity to dissolve cellulose or the cellulose product. This sometimes requires the use of a diluent, e.g., isobutyl acetate in making FA cotton [7].

Additional variables. Information is inadequate about the following important variables and aspects involved in making and using chemically modified cottons: degree of substitution, nature and distribution of substituents, yarn construction, fabric construction, blends with other fibers or yarns, application of softeners and other finishes, compressive shrinkage, and mechanical and heat treatments.

As some properties of cotton are improved by chemical modification, others are sometimes adversely affected. Acetylation, which greatly improves resistance to heat and to microbiological attack, may cause decreased elongation, tear strength, or abrasion resistance, depending upon the conditions of acetylation [40]. For some applications, decreased tear strength and abrasion resistance must be overcome. For PA cotton, these have been improved [66] by hot acetic acid swelling, hot acetic acid containing magnesium stearate, slack mercerization before acetylation; use of stearic acid in the acetylation mixture, application of softeners (calcium stearate, silicones, etc.), and compressive shrinkage of some PA fabrics.

All the chemically modified cottons thus far studied have been amenable to dyeing with some types of dye; hence dyeing seems to present no serious problem.

Depending upon the chemically modified cotton and the nature and scale of its manufacture, the intended end-use, and other circumstances, it is some-

times preferable to treat either the fiber, yarn, or fabric.

Treatment of fiber continuously and on a large scale has the advantage of greater versatility in that the product can be used as the fiber in filters, batting, stuffing, etc., and in making many types of yarn and fabric; also, one firm could do all the manufacturing, thereby taking advantage of all cost-saving opportunities.

Treatment of yarn or fabric instead of the fiber has advantages: fiber breakage and loss of short fibers are less serious, chemical and mechanical processing are simplified, and there is no chemical loss through reaction with waste.

Sometimes the properties of the end-product (fabric) are seriously affected by applying the treatment to fiber, yarn, or fabric. For example, the application of urea-formaldehyde, melamine-formaldehyde, and similar products to the fabric confers wrinkle resistance. Limited work indicates that greatly different effects may be obtained when the fabric is made from treated fibers or yarns.

Each chemically modified cotton has its own properties; hence each presents its own processing problems. The processing of PA and FA cottons is facilitated by using certain antistatic agents and by blending with untreated cottons [63]. Certain other chemically modified cottons, e.g., AM cotton and APO-treated cotton, can be processed moderately well without the use of antistatic and similar agents [66].

Whither Chemically Modified Cottons?

In 1925 [68], Taglioni ended a talk on chemically modified cottons with the following: "As we follow these changes we cannot but feel astounded at what can be obtained from a single cotton fiber, and what the future holds for us in possible permutations of cotton and of artificial fibers of vegetable origin. For the chemical laboratory remains the problem of building still further on the foundation of facts already known and bringing to completion the work which is already commenced. When this is accomplished an advance will have been made which will have far-reaching effect on the economic and technical development of both the chemical and textile industries."

Since this prediction, made 33 years ago, chemically modified cottons have—in spite of severe competition—made remarkable progress. There are reasons for predicting that they will continue to comprise an important segment of the textile and chemical industries.

The raw materials (cotton and many chemicals) are low-cost, widely available, and suitable for making new fibers; the cost of cotton and many chemicals should become even lower; cotton's well-known versatility as a textile fiber is matched by its versatility as a starting point for making new fibers; much of the high molecular weight and order of the cotton cellulose is retained in the modified cotton; and both the capital and operating costs of making some chemically modified cottons are low.

Literature Cited

1. Abrams, E. and Sherwood, N., *Am. Dyestuff Reptr.* **42**, 777–782 (1953).
2. *America's Textile Reptr.* **71**, No. 50, 20 (1957); **72**, No. 8, 31 (1958).
3. Bernoulli, A. L., Schenk, M., and Rohner, F., *Helv. Chim. Acta* **17**, 897–918 (1934); *J. Soc. Dyers Colourists* **50**, 410 (1934) (Abs.).
4. Bikales, N. M., Gruber, A. H., and Rapoport, L., *Ind. Eng. Chem.* **50**, 87–90 (1958).
5. Blouin, F. A. and Arthur, J. C., Jr., TEXTILE RESEARCH JOURNAL **28**, 198–204 (1958).
6. Buras, E. M., Jr., *Am. Dyestuff Reptr.* **46**, 929–930, 939–940 (1957).
7. Buras, E. M., Jr., Hobart, S. R., Hamalainen, C., and Cooper, A. S., Jr., TEXTILE RESEARCH JOURNAL **27**, 214–222 (1957).
8. *Ciba Rev.* No. 120, 2–32 (1957).
9. Compton, J., TEXTILE RESEARCH JOURNAL **27**, 222–231 (1957).
10. Cooke, T. F. and Roth, P. B., TEXTILE RESEARCH JOURNAL **26**, 229–242 (1956).
11. Cooke, T. F., Roth, P. B., Salsbury, J. M., Switlyk, G., and Van Loo, W. J., *Am. Dyestuff Reptr.* **46**, P585–600 (1957).
12. Cross, C. F. and Briggs, J. F., Brit. Patent 5016 (1907); *J. Soc. Dyers Colourists* **24**, 144 (1908) (Abs.).
13. Daul, G. C., Reinhardt, R. M., and Reid, J. D., TEXTILE RESEARCH JOURNAL **22**, 792–797 (1952).
14. Demint, R. J. and Hoffpauir, C. L., TEXTILE RESEARCH JOURNAL **27**, 290–294 (1957).
15. Elöd, E., Schmidt-Beilenberg, H., and Thoria, L., *Angew. Chem.* **47**, 465–468 (1934); *J. Soc. Dyers Colourists* **50**, 334 (1934) (Abs.).
16. Esteve, R. M., Jr., Wright, G. E., and Mack, P. B., "Investigation of Inorganic Salts and Oxides as Finishes for Cotton. III. Further Evaluation of Nine Promising Inorganic Compounds" (unpublished).
17. Fetscher, C. A. (to Cluett, Peabody and Co.), U. S. Patent 2,789,030 (April 16, 1957).

18. Fourt, L. and Elliott, H. J., TEXTILE RESEARCH JOURNAL **24**, 779–784 (1954).
19. Frick, J. W., Reeves, W. A., and Guthrie, J. D., TEXTILE RESEARCH JOURNAL **27**, 92–99 (1957).
20. Gilfillan, E. S. and Linden, L., TEXTILE RESEARCH JOURNAL **27**, 87–92 (1957).
21. Goldthwait, C. F., TEXTILE RESEARCH JOURNAL **21**, 55–62 (1951).
22. Goldthwait, C. F. and Guthrie, J. D., in *Matthew's Textile Fibers*, ed. by H. R. Mauersberger, 6th Ed., p. 219–256. John Wiley and Sons, New York (1954).
23. Gottlieb, I. and Jeffries, E., *Chem. Week* **80**, No. 11, 112, 114, 116 (1957).
24. Graham, R. T., TEXTILE RESEARCH JOURNAL **27**, 270–273 (1957).
25. Graham, R. T., Loibl, F., and Wiebush, J. R., TEXTILE RESEARCH JOURNAL **28**, 252–256 (1958).
26. Grant, J. N., McDonald, A. W., and Humphreys, G. C., TEXTILE RESEARCH JOURNAL **28**, 60–66 (1958).
27. Guthrie, J. D., *Am. Dyestuff Reptr.* **41**, P13–14, 30 (1952).
28. Hamalainen, C., Wade, R. H., and Buras, E. M., Jr., TEXTILE RESEARCH JOURNAL **27**, 168 (1957).
29. Haydel, C. H., Janssen, H. J., Seal, J. F., Vix, H. L. E., and Gastrock, E. A., TEXTILE RESEARCH JOURNAL **27**, 975–982 (1957).
30. Heberlein, G. and Weiss, E., TEXTILE RESEARCH JOURNAL **28**, 227–233 (1958).
31. Ikeda, S. and Okajima, S., *Textil-Praxis* **11**, 999–1002 (1956).
32. Janssen, H. J., DuPré, A. M., Haydel, C. H., Seal, J. F., and Vix, H. L. E., *Ind. Eng. Chem.* **50**, 76–79 (1958).
33. Karrer, P. and Kwong, S. C., *Helv. Chim. Acta* **11**, 525–529 (1928).
34. Karrer, P. and Wehrli, W., *Helv. Chim. Acta* **9**, 591–597 (1926).
35. Klein, E. and Snowden, J. E., *Ind. Eng. Chem.* **50**, 80–82 (1958).
36. Lawrie, L. G., Reynolds, R. J. W., and Ward, D., *J. Soc. Dyers Colourists* **56**, 6–17 (1940).
37. Marsh, J. T., *An Introduction to Textile Finishing*, 552 pp., Chapman and Hall, Ltd., London (1948).
38. New, A. A., *Textile Colorist* **59**, 403–408 (1937).
39. Nott, E. H. and Grant, J. N., TEXTILE RESEARCH JOURNAL **26**, 673–680 (1956).
40. Orr, R. S., Weiss, L. C., Burgis, A. W., and Grant, J. N., TEXTILE RESEARCH JOURNAL **27**, 966–975 (1957).
41. Pacsu, E. and Schwenker, R. F., Jr., TEXTILE RESEARCH JOURNAL **27**, 173–175 (1957).
42. Peacock, D. H., *J. Soc. Dyers Colourists* **42**, 53 (1926).
43. Philips, F. J., Segal, L., and Loeb, L. TEXTILE RESEARCH JOURNAL **27**, 369–378 (1957).
44. Pichlmayr, H., Brit. Patent 735,684, August 24, 1955.
45. Reeves, W. A., Drake, G. L., Jr., Chance, L. H., and Guthrie, J. D., TEXTILE RESEARCH JOURNAL **27**, 260–266 (1957).
46. Reeves, W. A., McMillan, O. J., Jr., and Guthrie, J. D., TEXTILE RESEARCH JOURNAL **23**, 527–532 (1953).
47. Reid, J. D. and Mazzeno, L. W., Jr., *Ind. Eng. Chem.* **41**, 2828–2831 (1949).
48. Reid, J. D., Mazzeno, L. W., Jr., and Buras, E. M., Jr., *Ind. Eng. Chem.* **41**, 2831–2834 (1949).
49. Reid, J. D., Mazzeno, L. W., Jr., Reinhardt, R. M., and Markezich, A. R., TEXTILE RESEARCH JOURNAL **27**, 252–259 (1957).
50. Reid, J. D. and Reinhardt, R. M., *Modern Textiles Mag.* **39**, No. 3, 61–68 (1958).
51. Reid, J. D., Reinhardt, R. M., and Kullman, R. M. H., TEXTILE RESEARCH JOURNAL **28**, 242–251 (1958).
52. Reinhardt, R. M., Fenner, T. W., and Reid, J. D., TEXTILE RESEARCH JOURNAL **27**, 873–878 (1957).
53. Reinhardt, R. M., Reid, J. D., and Daul, G. C., TEXTILE RESEARCH JOURNAL **26**, 1–9 (1956).
54. Reinhardt, R. M. and Tallant, J. D., TEXTILE RESEARCH JOURNAL **27**, 24–29 (1957).
55. [Rheiner, A.] Chemische Fabrik vorm Sandoz. Brit. Patent 363,435 (1930).
56. [Rheiner, A.] Chemische Fabrik vorm Sandoz. Swiss Patent 204,046 (1939).
57. Salsbury, J. M., *Modern Textiles Mag.* **38**, No. 4, 82–86, 103 (1957).
58. Schneider, J., *J. Soc. Dyers Colourists* **23**, 78–80 (1907).
59. Schuyten, H. A., Weaver, J. W., Frick, J. G., Jr., and Reid, J. D., TEXTILE RESEARCH JOURNAL **22**, 424–432 (1952).
60. Schwenker, R. F., Jr. and Pacsu, E., *Ind. Eng. Chem.* **50**, 91–96 (1958).
61. Sen, M. K. and Ramaswamy, M., *J. Textile Inst.* **48**, T75–80 (1957).
62. Segal, L., Philips, F. J., Loeb, L., and Clayton, R. L., Jr., TEXTILE RESEARCH JOURNAL **28**, 233–241 (1958).
63. Sloan, W. G., Sens, C. L., and Buras, E. M., Jr., TEXTILE RESEARCH JOURNAL **27**, 796–802 (1957).
64. Smith, L., *America's Textile Reptr.* **72**, No. 2, 18 (1958).
65. Soffer, L. M. and Carpenter, E., TEXTILE RESEARCH JOURNAL **24**, 847–852 (1954).
66. Southern Regional Research Laboratory, Agricultural Research Service, U. S. Department of Agriculture, unpublished results.
67. Steele, R., *Am. Dyestuff Reptr.* **46**, 329–335 (1957).
68. Tagliani, G., *J. Soc. Dyers Colourists* **41**, 165–168 (1925).
69. Takagi, T., Brit. Patent 750,702, April 1, 1954; *J. Appl. Chem. (London) Abs.* **7**, ii, 91 (1957).
70. Taylor, J. L. and Owens, E. D., TEXTILE RESEARCH JOURNAL **24**, 810–819 (1954).
71. Teszler, O., Wiehart, H., and Rutherford, H. A., TEXTILE RESEARCH JOURNAL **28**, 131–135 (1958).
72. Tripp, V. W., Giuffria, R., and deGruy, I. V., TEXTILE RESEARCH JOURNAL **27**, 14–24 (1957).
73. Unruh, C. C. and Kenyon, W. O., TEXTILE RESEARCH JOURNAL **16**, 1–12 (1946).

74. Urquhart, A. R., TEXTILE RESEARCH JOURNAL **28**, 159–169 (1958).
75. Vickerstaff, T., *Am. Dyestuff Reptr.* **47**, 33–38 (1958).
76. Wolfrom, M. L., Sowden, J. C., and Metcalf, E. A., *J. Am. Chem. Soc.* **63**, 1688–1691 (1941).
77. Woodhead, A. E., *J. Soc. Dyers Colourists* **46**, 69–74 (1930).
78. Zilahi, M. and Móczár, E., *Faserforsch. u. Textiltech.* **8**, 192–195 (1957).
79. Zilahi, M. and Oswald, L., *Magyar Textiltechn.* **6**, 204–207 (1956).

Some Concepts of Cotton Research[1]

George S. Buck, Jr.

National Cotton Council of America, Memphis, Tennessee

COTTON has many research programs, guided by many interests and carried out by many different individuals, agencies, and organizations. This diffusion, both geographical and functional, reflects the same basic characteristic of the cotton industry itself. Yet in research the industry comes closer to general agreement on aims and objectives than on any other subject. This could mean either that research necessarily follows certain logical patterns, or that research escapes some of the pressures and counter-currents that beset the industry as a whole. In any case, the purpose of this paper is to present some of the concepts upon which the cotton industry bases its efforts in research.

It should be recognized that any turmoil and confusion apparent in the cotton picture is only the outward sign of a sometimes reluctant technological revolution in a vast, complex agricultural industry. This industry involves millions of individuals, many diverse and sometimes conflicting interests, years of tradition, lifetimes of habits and practices, and no few prejudices. The transition of such a great agricultural-industrial complex into an efficient, technologically competitive modern industry must necessarily be painful. Yet such a transition is an absolute essential for survival in an age in which science has brought us to the very frontiers of space.

The cotton industry's moves toward modernization of facilities, mechanization of operations, and the discard of obsolete practices show a determination to meet the challenge of this age of science. Above all, its efforts to expand research on cotton, both through increased support from publicly financed research agencies and through programs which the industry itself will underwrite, mean the industry has accurately assessed its problems and determined its course. What, then, are the goals toward which this greater effort in cotton research will be directed?

Let's start with the over-all objective: to increase the use of cotton and its products and byproducts. This can be done in two ways: by developing new uses for cotton or by maintaining or expanding the use of cotton in its present markets. In either case, cotton must be competitive in price, quality, and promotion. In other words, cotton would have exactly the same problems in a new use as in any of its present uses, only to a greater extent because a new use would have to be developed and cotton would not have the benefits of an "established" position. Recognizing this truth, the cotton industry has pointed its research programs at two of the fundamentals of competition: price and quality. Research which lowers *cost* can lead to a more competitive price. Research which improves quality or develops entirely "new" qualities increases the *usefulness* of cotton. Improvement in both factors—price and quality—provide a broader base for the third dimension of competitive strength: promotion.

If the *price* of cotton is to be more competitive, it would seem that the cost of its production should come down. Can this cost be reduced, and how?

First, we must note that there is no such thing as *a* cost of producing cotton. This year much publicity was given to one grower who put a substantial

[1] Presented at the 28th Annual Meeting of the Textile Research Institute, New York City, March 14, 1958.

acreage in the soil bank, overplanted his allotment on other acreage, paid a penalty which approached a million dollars, and still showed a profit. Contrast his unusual case with the many farmers who, beset by terrible weather conditions and fierce insect attacks, almost "lost their shirts" at double his cost. Neither of these situations provides us with a suitable cost figure. We can, however, examine certain production costs and cost-producing losses as *averages* for the industry, and then see how their reduction would affect cotton's cost relative to the competition.

Cotton passes through production stages in becoming a consumer product rather comparable to those in manufacturing synthetics. Where the artificial fiber uses chemicals and raw materials, cotton depends on seed and soil, water and fertilizer. The chemical reactions which lead to synthetic fiber development parallel processes controlled by herbicides and insecticides in cotton production. Under these protective influences nature forms the fiber, as man shapes the synthetic in the extrusion process.

The fibers themselves—natural and artificial—pass through nearly the same operations of marketing and processing. Only in the early stages are there significant differences which mean real opportunities for cotton.

On the basis of an average for the whole industry, some of the important losses in growing cotton have been estimated. Three of these, in terms of production losses and control measures, are insects, disease, and weeds.

On the average of the whole crop, losses due to insects, and the expense of their partial control, amounts to more than 4¢/lb. One insect, the boll weevil, destroys more fiber some years than the entire U. S. production of rayon. For certain areas in the Southeast, the boll weevil may add 12¢ or more to the costs of producing the average pound of cotton.

On the average of the whole crop, estimates show cotton diseases add 4¢ to every pound of cotton produced. As with insects, the losses to disease are especially severe in certain areas of the Belt. But on the average—and this can only be figured on the average—diseases appear to be adding as much or more than insects to the cost of cotton.

Weeds contribute other costs, either by their depressing effect on yield and quality or through the cost of their control. The yearly total cost, running in hundreds of millions of dollars, may again average 4¢ on every pound of cotton produced. Thus weeds take their place with insects and disease as another big destructive, cost-building factor in cotton growing.

Mainly, insects, diseases, and weeds act to reduce yield. But many other factors also affect yield. The cotton plant itself—for reasons not well understood—normally sheds about ⅔ of its bolls prematurely. The weather may reduce yield. On the other hand, fertilizer, irrigation, the development of improved varieties, and other practices have a *positive* effect on yield.

With yield as a measure of productivity and roughly an inverse measure of cost, what can be done? In 1957 the Belt-wide yield was 390 lb./acre, up about 90 lb. from the 1946–1955 average. But some parts of the Cotton Belt averaged less than 250 lb./acre, while others—and these are *averages*—hit levels of 1100 lb./acre. Marks for individual farms were recorded at 1500 or more pounds per acre.

The benefits of mechanization can be realized at almost every stage of production and harvesting. In some operations—cotton picking for example—a single machine may do the work of 50 men. This is a part of efficiency. While it takes money to farm efficiently—generally more in land, capital, management, chemicals, and water—costs per pound can be materially reduced. A measure of this is the steady downward trend over the last twenty years in the man-hours per acre employed in growing cotton (see Table I).

Can the cost of producing cotton be significantly reduced? In reaching its answer the cotton industry adds up many factors. One is the opportunity for research—in controlling insects, disease, and weeds—in increasing yield—in mechanization. One is the

TABLE I. Trend of Man-Hours in Production of Cotton

Year	Man-hours per bale
1925	271
1935	234
1945	175
1946	170
1947	150
1948	137
1949	130
1950	128
1951	121
1952	116
1953	105
1954	101
1955	93
1956	94

TABLE II. Rayon Staple Cost of Production

Wood pulp	9.7¢
Chemicals	4.0¢
Labor	3.1¢
Depreciation	3.5¢
Water, power, etc.	1.3¢
Selling and administrative	1.1¢
Freight	1.0¢
Other	1.9¢
Total	25.6¢

tremendous *scope* for many types of science—biology and its divisions as well as the physical sciences and engineering. Another is the demonstration that the average cost of the industry is well above levels that can be achieved *today*. The answer to the question is yes—definitely yes.

Can cotton's closest competitors in price match its potential for reduction in cost?

Table II shows an analysis of costs which were typical for rayon early in 1957. The net cost for this artificial fiber was about 26¢/lb. The selling price of rayon in recent months has been around 31¢/lb. There is good reason to believe that—at this cost level—the era of really important cost reductions in rayon is past. The recent prices of rayon, the statements of top executives of the industry, and the earnings' reports of rayon firms tend to confirm this belief.

Therefore, in this first concept of cotton research —research directed toward cutting the cost of producing the fiber—there is every reason to believe that the opportunities for cotton are truly significant.

There are other potentials for shrinking costs in the marketing and processing of cotton. But these costs are so interdependent on quality that they can best be discussed in that relationship. Let us consider some concepts of cotton quality research.

Cotton—like other textile fibers—is a raw material. It is a raw material which allows for a certain amount of selection by those who will fabricate it into a product. It must also command the choice of a manufacturer from those other available fibers that could be used to make the same product. Finally, cotton, in the form of some textile article, must earn the preference of the ultimate consumer.

Thus cotton must—not considering price—possess the qualities that will influence fiber selection at two levels: first by the mill, and then by the ultimate consumer. This is no new concept, but it is at least an important one for all of us in the cotton industry to keep well in mind.

How does quality affect the selection of cotton by the mill? In many cases the first consideration is the product itself, the intended use of that product, and the properties that use demands. When cotton fits the use requirements better than other fibers, the mill bases its selections from among qualities of cottons on several considerations. Essentially these add up to making the best possible product at the lowest possible cost, although the emphasis on quality or cost will differ with individual mills. In all cases, however, it is important for the mill to know *how* a given lot of cotton will perform, and for cotton of a given quality or market value to perform as expected.

To an increasing extent, today's highly competitive industry has placed greater emphasis on processing costs. Job assignments, speeds, and the size of "packages" have all increased. This in turn has increased the demand that the fiber process efficiently in the mill. A trend toward higher qualities of cotton has resulted.

Under these circumstances, any failure of higher quality cottons to reflect their market value in better processing results, at the least, in dissatisfaction in the mill and an increased cost for cotton products. At the worst, from the cotton point of view, it provides an incentive to substitute other staples for cotton. Unfortunately it would appear that, for a variety of reasons, the established criteria of quality used in our raw cotton marketing system do not consistently reflect the spinning and weaving performance of cotton.

The only bright spot in the picture is that we can, by understanding the vexing problem, grasp the full concept of where cotton research on quality *and* price should be concentrated at this stage of marketing. We reach the following conclusions.

First, research should be directed toward a more complete identification and measurement of those fiber properties which determine the manufacturing performance of cotton and its usefulness in textile products. This would be the first step in restoring the ability of mills to select the most competitive cottons for their purposes.

The second step should be the development of rapid, accurate, commercially practical methods of measuring cotton's true use value, including its spinning performance. To exert their full influence these methods must then be added to the criteria which establish cotton's market value.

Thirdly, research should be directed toward those aspects of cotton quality which determine good mill performance. Mainly this means improvement in fiber properties such as length, length uniformity, strength, maturity, and freedom from certain types of trash. But it also means research directed toward the preservation of those valuable qualities through *all* the stages of fiber production, marketing, and processing.

The list of specific research studies in this field is long, giving the fiber scientist a fruitful field of investigation. The problems range from the fundamental to direct mill applications. Studies of the Textile Research Institute have been particularly helpful in the efforts to relate the properties of single fibers and fiber assemblies to processing performance. It seems certain that research in fields ranging from cotton genetics to fiber instrumentation can significantly set up the levels of cotton's mill performance and thus reduce another element of its cost.

To a very large extent, the factors of quality which concern cotton's first customers—the mills—mean little to the ultimate consumer. The effects of fiber qualities on yarn appearance, and in some cases on the strength of yarns and fabrics, may be more or less important to the consumer, depending on the product. But for the most part consumers have their own criteria of quality, and they concern themselves with what the product is, not how it got that way.

The second concept of quality research in cotton stems directly from the wants of the consumer. Here the cotton industry directs its planning backward, *from* the quality, function, or performance the consumer desires, *to* the properties of fiber, fabric, or finish which will yield that consumer quality.

Since the idea is to "give the customer what she wants" the logical approach calls for the factual, objective determination of consumer likes and dislikes. For years the cotton industry has made extensive use of marketing research as the basis for planning research on improved products. These studies, market by market and use by use, record and tabulate consumer preferences for cotton and competitive materials. They analyze such factors as price, quality, promotion, merchandising methods, consumer habits and traditions, and fashion. They measure the size of markets, competitive pressures in those markets, and trends in the consumption of cotton and competing materials.

Let's take a look at how all this wealth of information shapes the consumer quality research programs of cotton. We will note that these data, in an industry whose product goes into hundreds of different articles, dictate a broader approach than might be the case with the manufacturer of just a few products.

From retail contacts, consumer preference surveys, trade information, and other sources, specific qualities important to consumers in various textile products are determined. Those in which improvement would strengthen cotton's competitive position are ranked according to their importance. Then, through a combination of these *qualities* with the *quantities* of cotton and competing fibers used in markets where they are significant influences on consumer choice, a weighted list of cotton's needs is obtained. Note that the approach to developing improved *products* is therefore by improving *qualities*. While this may seem indirect, some examples may show that it is the most productive course for the cotton industry.

In a comprehensive and detailed analysis made by the National Cotton Council, the consumer qualities important in 114 end-uses were determined. Forty-five different qualities were considered. The ranking of these produces a list of priorities, not for research studies, but for initial research objectives (Table III).

Each of the initial objectives—which are still given in the consumer's own language—is subjected to a technical analysis. Crease resistance, for example, depends largely on certain basic fiber properties, mainly physical, with the elastic characteristics being most important. Warmth in textiles depends on fabric thickness, and the maintenance of the desired "bulk without weight" in turn requires a resilient fiber. Thus those important consumer qualities depend on essentially the same basic elastic property of the fiber—resilience.

Luster, on the other hand, stems mainly from the shape and surface characteristics of the fiber, yarn, and fabric. We find one approach to soil resistance related to the same characteristic.

For cotton, the type of analysis which has been only sketched here leads to a convenient grouping of consumer quality research objectives that greatly simplifies the research approach which at the same time permits a concentration of effort and yields a multiplication of the benefits of success. Twenty-

eight of the 45 qualities studied fall logically into four groups, which now become specific objectives of consumer quality research on cotton (Table IV). These are resilience properties, chemical properties, shape and surface properties, and tensile strength.

These groups of course represent fairly broad and basic approaches, and they break down to many separate fundamental and applied studies. Under resilience properties, for example, the National Cotton Council study lists 41 different projects in 6 project areas. Obviously these are only a start in a program which will change shape as developments occur. But this grouping provides a method of moving toward our objectives which is, we believe, the most logical and systematic way to accomplish our purposes and to make each cotton research dollar effective.

The Southern Laboratory of the U. S. Department of Agriculture has pioneered in the chemical modification of cotton, and its developments have a really great potential for the cotton industry. Many of us believe that the work of the Southern Laboratory is bringing closer the day of the "all-purpose cotton finish"—one that will be crease resistant, fire and mildew resistant, dimensionally stable, and water and soil repellent. Who can doubt that such a multi-purpose cotton will have a tremendous impact on the textile market!

The effects of cotton research in general—both on quality and price—on not only the textile market but the prosperity and the future of textile manufacturers, deserves some consideration. Is competition among fibers, and research supporting that competition, good or bad for the textile industry? What direct contribution does research on cotton make to the strengthening of the textile industry?

First let's recognize that interfiber competition is itself the great stimulus for research on cotton just as it is on man-made fibers. The plain fact is that

TABLE III. Quality Improvements Which Would Strengthen Cotton's Competitive Position

Consumer qualities	Estimated size of market affected (1,000 bales, cotton bale equiv.) All materials	Held by cotton	Held by other materials
Luster	8,837	5,072	3,765
Soiling resistance	8,240	4,118	4,122
Stain resistance	8,180	3,741	4,439
Soft colors	5,978	2,647	3,331
Crease resistance	5,258	3,175	2,083
No ironing	4,924	3,220	1,704
Quick drying	4,283	2,527	1,756
Draping qualities	4,187	2,134	2,053
Warmth	4,179	2,532	1,647
Fire resistance	3,972	1,230	2,742
Water repellence	3,324	1,240	2,084
Abrasion resistance	3,155	1,741	1,414
Fraying resistance	3,075	1,930	1,145
Permanent crispness	2,771	2,016	755
Low bulk	2,718	666	2,052
Vivid prints	2,687	1,515	1,172
Heat resistance	2,657	502	2,155
Light weight	2,265	457	1,808
Resiliency	1,790	518	1,272
Tensile strength	1,753	511	1,242
Slipperiness	1,706	376	1,330
Mildew resistance	1,448	421	1,027
Flex life	1,402	251	1,151
Hand	1,308	274	1,034
Sheerness	1,285	504	781
Rustling	1,242	403	839
Clinging resistance	1,161	547	614
Linting resistance	1,103	523	580
Snagging resistance	1,101	461	640
Elasticity	1,013	377	636
Insulating properties, electric	946	104	842
Insulating properties, thermal	875	—	875
Pilling resistance	478	152	326
Chemical resistance	422	297	125
Static electricity resistance	411	96	315
Weathering resistance	302	261	41
Fast dyes	255	242	13
Coolness	182	157	25
Elongation	136	88	48

TABLE IV. Use-Qualities Grouped by Technical Approach

Group I—Resilience properties

Soft colors	Abrasion resistance
Crease resistance	Resilience
No ironing	Flex life
Draping qualities	Hand
Warmth	Insulating properties—heat
	Elasticity

Group II—Chemical properties

Stain resistance	Heat resistance
Quick drying	Mildew resistance
Fire resistance	Insulating properties—electrical
Chemical resistance	Weather resistance
Water repellency	

Group III—Shape and surface properties

Luster	Vivid prints
Soil resistance	Slipperiness

Group IV—Tensile strength

Tensile strength	Light weight
Low bulk	Sheerness

no fiber can long maintain its position—or even a place—in the textile market unless its price and performance meet the competition. Expansion of the textile market—which we certainly hope will continue over the long run—may delay but will not prevent the demise of fibers that fail to meet this test.

The recognition by most fiber producers and producing groups of the need to employ research to remain in business leads to a steady improvement in textile materials, to entirely new products and qualities, and thus to a dynamic textile industry. Just one example of a product of competitive research—the wrinkle resistant, easy care cottons—testifies to the way research can be applied to give our industry new products and new merchandising possibilities.

There is a good question on the extent to which the manufacturing segment of this industry can afford to stand by and watch the fiber producers battle it out. While the results of this conflict are bound to help manufacturers over the short run, a trend in the long run to the artificial fibers and related materials has some implications which should command the thoughtful consideration and perhaps deep concern of all textile manufacturers. Let us examine some recent developments to see why.

Synthetic fibers first appeared on the textile scene in the form of continuous filaments. As these filaments improved they displaced some spindles. The character of filament fabrics somewhat limited their use, however, and manufacturers took some consolation in an apparent trend to cut staples. But how does the situation look today? Filament yarns are steadily approaching spuns in texture, taking over more traditional spun yarn uses. They are even being knit into sweaters.

Just recently a man who was for over thirty years an official of one of the large rayon producers suggested that we are now in the period when filament yarns will be substituted for fibrous types. He went on to say that the next step would be the substitution of sheet materials, either cast, bonded, or molded, for textile fabrics. Can we see such a trend starting now?

The "nonwovens" might be cited as a first step away from conventional textiles. Their use has increased steadily, as has their quality. Today they probably cause textile men little alarm, but how about 5 or 10 years from now?

Plastic film and sheetings, which have already displaced a substantial volume of textiles, now seem limited to certain uses. But where will they stop, when science has given them breathing properties and a more clothlike texture?

What is the future of the new felt-like synthetics which require no weaving? How about the paper fabrics which incorporate synthetic fibers and which get more textile-like each year? Finally, what use are some of the major fiber producers planning to make of those entirely new methods of extruding, combining, and bonding fibers on which they are known to be experimenting?

The *pace* of research and development is accelerating tremendously in all fields. Is there anyone today willing to predict where it will stop? Will an unchecked trend toward the plastic fibers and related products of the laboratory mean the end of the textile industry as we know it?

These are interesting questions, not easy to answer. But any new products that would take the place of textiles would of course have to meet the tests of competitive performance and competitive price. In the cotton industry we are encouraged to believe that our opportunities to reduce cost and to improve and extend quality through research can enable cotton to hold its own even with the "nontextile" competition which science may bring forth. Perhaps manufacturers also can be encouraged by the thought that, no matter what new form the synthetics take, cotton will always have to be spun and woven in their mills.

Ultraviolet Absorbers[1]

R. A. Coleman and W. H. Peacock

American Cyanamid Company, Research Division, Bound Brook, New Jersey

IN ORDER to lay a proper background for the discussion of ultraviolet absorbers, we will first consider certain properties of ultraviolet light. The ultraviolet light with which we are concerned is a small invisible portion of sunlight which we believe is most responsible for the destructive action of sunlight exposure, such as the fading of dyes, the yellowing and embrittling of plastics, and the sun tanning of human skin.

The sunlight reaching the earth (Figure 1) consists of a continuous spectrum of radiant energy having wavelengths between 300 and 5000 mμ. About 45% of this light lies between 400 and 700 mμ and is visible to the eye as white light. When broken down into its components as in a rainbow, white light yields the colors violet, blue, green, yellow, orange, and red, which represent increasingly longer wavelengths of light.

Radiant energy having wavelengths longer than 700 mμ is invisible and is found in the infrared region. Since these rays tend to warm whatever they irradiate, they are considered as radiant heat.

The shorter wavelengths; that is, between 300 and 400 mμ, are also invisible but are called ultraviolet light. It is this ultraviolet light, which represents only about 5% of the total sunlight, that is the focal point of this discussion.

From what is known about ultraviolet light, it is no wonder that it is suspected as a prime factor in the photochemical attack upon all kinds of organic material. Light consists of bundles of energy, called photons, that have wave characteristics. The photons with the shortest wavelengths have the most energy. Consequently, those photons in sunlight with the greatest energy are found in the ultraviolet region. Ultraviolet photons have more energy than many of the molecular bonds in organic compounds. When absorbed by a molecule, the photons can initiate chemical reactions that can be viewed as photodegradation.

Experimentally, photodegradation has been reported to be caused by energy from both the ultraviolet and the visible wavelengths of light [2, 4]. This additional destructive contribution by visible light poses a special practical problem in the development of screens to protect against these energies.

A screen is an optical filter that absorbs certain wavelengths of light and allows the rest of the spectrum to pass on through. A screen that absorbs ultraviolet light might well be colorless. Any screen, however, that removes *both* ultraviolet and a portion of the visible spectrum must necessarily be colored, a fact that is usually undesirable. As an example, the amber-colored screens currently used in show windows modify the appearance of objects behind them. Colorless ultraviolet absorbing screens, on the other hand, can offer protection against ultraviolet light but none against visible. They also can be very useful in separating the effects of visible and ultraviolet light on substances.

We have made some preliminary studies of the fading of dyes and the weakening of fabrics behind such an ultraviolet absorbing screen. The screen was made of cellulose acetate. This film was designed to absorb strongly in the ultraviolet region and to transmit highly in the visible region. The spectrophotometric transmission curve (Figure 2) sloped sharply upward, passing through the 45% transmission level at 400 mμ. The small amount of

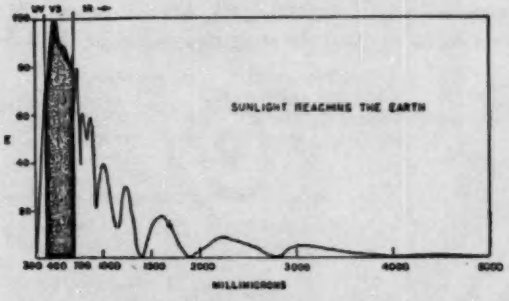


Fig. 1. Spectral distribution of sunlight reaching the earth on a clear June day. E is relative energy.

[1] Presented at the 28th Annual Meeting of the Textile Research Institute, New York City, March 13, 1958.

absorption between 400 and 430 mμ imparts a very slight yellow cast that is not always easy to see. Normal cellulose acetate film has very little absorption, as shown by the upper curve (Figure 2). Both curves level off at about 90% because of the reflection and scattering of light from the surfaces.

Our experimental procedure consisted of exposing to direct light two samples of dyed fabric. One sample was covered with the ultraviolet absorbing screen, and the other was covered with a clear film that did not absorb ultraviolet light. The difference between the fadings of a dyeing behind the screens is due to ultraviolet light. This difference also indicates the decrease in the rate of fading that can result by eliminating the ultraviolet light.

Fade-Ometer Exposures

As a first step, Fade-Ometer exposures of 81 direct cotton dyeings and 76 wool dyeings were made behind each film. Each of the 314 samples was exposed for various lengths of time, and fading versus time curves were drawn. The fading data were taken as Munsell notations, which were converted by the Nickerson index of fading formula [3] to give the amount of fade in Judd units. From the fading versus time curves, we were able to read the number of Fade-Ometer exposure hours required to obtain a perceptible fade of three Judd units for each dyeing under each film (Table I).

The cotton dyeings were placed in their respective light fastness groups, and the average hours for fading of each group plotted as bar graphs (Figure 3). In each case the cross-hatched or right hand bar of each pair represents the protected exposures. The dotted bar represents unprotected exposures. The L0, L1, L2, etc. along the horizontal axis are the AATCC light fastness ratings. The average times for fading in every group are substantially increased by screening out the ultraviolet light. Particularly noteworthy in this respect are the most light-fast dyes. A similar bar graph (Figure 4) for the wool dyeing data (Table II) indicates a similar increase in time to fade when the ultraviolet light is removed.

Those dyeings most improved by ultraviolet light protection are those that normally have the highest light fastness ratings. The L4 direct cotton dyeings are improved 61%; the L1 dyeings are improved 50%. The average improvement in the L5 wool dyeings is 600%, while the corresponding figure of the L1 wool dyeings is 100%.

If ultraviolet radiation were the sole cause of fading, then no fading should take place under the ultraviolet screen. Any fading behind the ultraviolet screen, therefore, is caused by visible light. For most of the fugitive dyes, the ultraviolet screen has very little effect. These dyes are faded much more by the visible portion of sunlight than ultraviolet. There are two dyes that are only slightly affected by

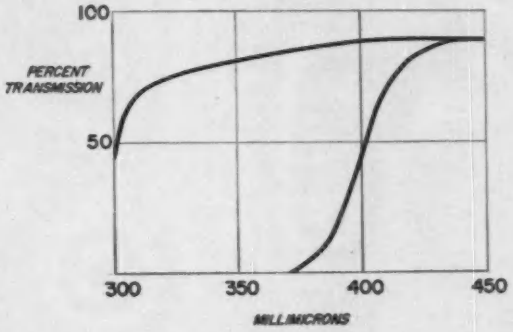


Fig. 2. Spectrophotometric curves of cellulose acetate films 0.012 in. thick. The lower curve is for a film containing 0.55% of 2,2'-dihydroxy-4-methoxybenzophenone.

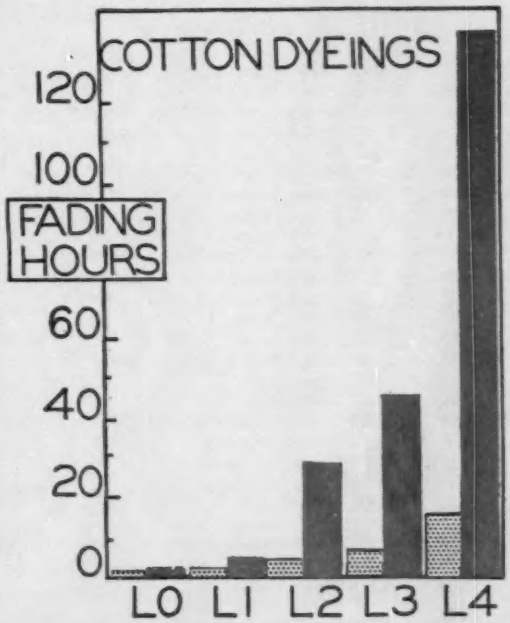


Fig. 3. Fading data of 79 different cotton dyeings. The bars showing the average number of Fade-Ometer hours for a 3-Judd color change for dyeings in each light fastness group are dotted for 'not protected' and cross-hatched for 'protected' from ultraviolet light.

TABLE I. Fading of Direct Dyes on Cotton Behind Films With and Without Ultraviolet Absorber

Conc., %	Dyeing†	Fade-Ometer hours to 3 Judds		Arizona Langleys to 3 Judds		Arizona Fading by UV portion, %
		N*	P**	N*	P**	
.25	Calcomine Brilliant Rubine B	0.57	0.75	35.0	40.0	12
3.00	Calcomine Brilliant Rubine B	.66	1.02	36	62	41
.125	CI Direct Violet 9	.71	.96			
.25	CI Direct Violet 33	.78	1.16			
.0625	CI Direct Blue 6	.80	.86	12	45	73
.125	CI Direct Blue 8	.80	.95	59	69	
.25	CI Direct Blue 1	.87	1.1			
.25	CI Direct Yellow 11	.89	10.23	48.4	406	88
.25	CI Direct Violet 22	.89	1.1	64	74	13
.25	CI Direct Yellow 6	.91	51.1	39.5	946	96
.125	Calcomine Blue RW	.91	1.1	33	43	23
.0625	CI Direct Blue 15	.96	1.3			
.25	CI Direct Brown 1	.97	1.4	110	129	15
.25	CI Direct Red 2	1.08	2.6	483	1044	54
.25	CI Direct Red 10	1.13	1.8			
.25	CI Direct Red 10	1.4	2.1	133	552	76
.25	CI Direct Brown 31	1.6	3.2			
.25	CI Direct Blue 2	1.6	2.4			
.25	CI Direct Black 9	1.6	2.4			
.25	CI Direct Red 13	1.7	4.8	67	351	81
.25	CI Direct Red 24	1.8	3.2	148	154	4
.25	CI Direct Black 38	1.8	2.4			
.25	CI Direct Black 38	1.9	2.7			
.25	CI Direct Red 23	1.9	2.4			
.25	Calcomine Green 5GSC	1.9	5.1			
.25	CI Direct Brown 59	2.0	3.5			
.25	CI Direct Green 12	2.0	3.8	67	139	52
.25	CI Direct Blue 47	2.0	3.6			
.25	CI Direct Black 80	2.1	3.1	227	469	52
.25	CI Direct Green 6	2.1	4.5	176	210	16
.25	CI Direct Brown 2	2.1	7.0			
.25	CI Direct Green 8	1.9	4.1			
.25	CI Direct Green 8	2.2	4.8	184	218	16
.25	CI Direct Black 4	2.2	3.8	124	170	27
.25	CI Direct Black 4	2.3	3.6	110	113	2
.25	Calcomine Brilliant Green Y	2.3	4.0			
.25	CI Direct Blue 24	2.5	4.2	87	152	43
.25	CI Direct Red 26	2.6	4.0			
.25	CI Direct Orange 1	2.6	19.1	610	729	16
.25	CI Direct Green 1	3.0	4.5			
.25	CI Direct Yellow 26	3.0	9.5			
.125	CI Direct Violet 51	3.1	7.3			
4.0	CI Direct Black 38	3.2	12.0			
.25	CI Direct Orange 34	3.0	61.2	469	1920	76
.25	CI Direct Orange 34	3.2	128.2	143	9465	98
.25	CI Direct Orange 29	3.4	15.5	339	849	60
.25	CI Direct Violet 1	3.5	7.8			
.25	CI Direct Black 51	3.5	5.5			
.25	CI Direct Orange 15	2.9	40.1	145	1757	92
.25	CI Direct Orange 15	3.7	19.4	554	1942	71
.25	CI Direct Orange 15	3.8	38.8	435	1706	75
.125	CI Direct Yellow 28	3.7	6.2			
.25	CI Direct Yellow 28	3.9	7.6	508	771	34
.125	CI Direct Yellow 12	4.3	40.1	99	1282	92
.25	CI Direct Red 1	4.3	43.8	110	1662	93

† Duplicate listings of dyeings at a given concentration are due to dyes of different sales types.
* N column, the samples were exposed behind an ordinary cellulose acetate film.
** P column, the samples were exposed behind a cellulose film containing ultraviolet absorber. See Figure 2.

TABLE I—Continued

Conc., %	Dyeing†	Fade-Ometer hours to 3 Judds		Arizona Langleys to 3 Judds		Arizona Fading by UV portion, %
		N*	P**	N*	P**	
.25	CI Direct Orange 37	4.5	76.8	386	4050	90
.25	CI Direct Brown 49	4.6	12.9	321	1457	78
.25	CI Direct Yellow 50	4.8	33.2	610	2680	77
.125	CI Direct Brown 95	5.1	33.2	763	2280	67
.125	CI Direct Red 75	6.0	35.8	1480	2050	28
4.0	CI Direct Black 9	6.1	20.8	1219	1272	4
.25	Calcodur Resin Fast Brown G	6.2	29.1	508	2720	81
.25	CI Direct Blue 78	6.2	48.4	829	2730	70
.25	CI Direct Red 81	7.2	53.7	670	2050	67
.25	CI Direct Yellow 4	7.4	64.6	560	4390	87
1.0	CI Direct Red 75	7.9	43.1	942	1922	51
.25	CI Direct Blue 76	8.0	38.1	1480	2360	37
.25	CI Direct Blue 86	8.1	96.9	255	758	66
.25	CI Direct Red 80	8.1	17.8	767	1314	42
.25	CI Direct Orange 72	8.5	83.0	1152	3340	65
.25	CI Direct Green 27	9.0	43.8	423	2796	85
.25	CI Direct Red 94	10.4	116.2	1220	3400	64
.25	CI Direct Blue 198	11.9	139.0	2038	4210	52
.125	CI Direct Blue 66	12.4	214.8	556	8890	37
.25	CI Direct Blue 71	14.2	157.5	970	5160	81
.25	Calcodur Gray 2GFL	14.5	84.4	1510	3917	61
.125	CI Direct Blue 67	16.5	196.9	1060	12600	92
.25	CI Direct Red 79	19.8	136.7	1360	3618	62
.25	CI Direct Blue 80	20.0	73.3	2039	5037	60
.25	CI Direct Red 83	23.9	98.4	1570	2640	41
.25	Calcodur Blue 2GFL	27.8	94.4	2260	5600	60

visible light but are extremely sensitive to ultraviolet light. They are Direct Yellow 6 and Direct Yellow 11, both of which were not included in the average. In general, the light fastness of dyeings fugitive to visible light cannot be greatly improved by screening out the ultraviolet radiation.

It is interesting to note that these results parallel those published by McLaren two years ago [4], even though he used a screen that absorbed appreciably more visible light than did our screen.

Sunlight Exposures

As in all color fading work, the question arises—will the Fade-Ometer exposures correlate with sunlight exposures? The Fade-Ometer carbon arcs emit light that is richer in ultraviolet radiation than sunlight, and therefore might give uncorrelatable results. Accordingly, many of these same cotton dyeings were exposed to sunlight in Arizona in August 1957 so that the fading results could be compared with those obtained in the Fade-Ometer.

As only one exposure period was contemplated for each sample, the previous Fade-Ometer data were used to estimate the amount of Arizona exposure needed. This was done by grouping the dyeings with a blue wool standard of about equal Fade-Ometer fastness. Each group sent to Arizona was exposed until the blue wool standard was perceptibly faded. The color change for these sun-exposed samples was calculated from Colormaster readings. The number of Langley units of sunlight energy required to give a color change of three Judd units for each dyeing (Table I) was calculated by proportionally adjusting the number of Judd units coming through glass for the exposure period. That is,

$$\text{Langleys for 3-Judd change} = 3 \times \frac{\text{actual color change}}{\text{number of Langleys}}$$

In this work, about 64 Langley units were found in one hour of bright sun (1 UV sun hour) under glass. The transmission of light through the clear plastic is about the same as that through glass; therefore, the Langley energy data under glass is used in the above calculations.

The data from the sunlight exposures were found to correlate qualitatively with the results from the

TABLE II. Fading of Acid Dyes on Wool Behind Films With and Without Ultraviolet Absorbers

Conc., %	Acid dye*	Fade-Ometer hours to 3 Judd N	P	Conc., %	Acid dye*	Fade-Ometer hours to 3 Judd N	P
.5	CI Acid Blue 75	0.4	0.9	.5	CI Acid Red 134	6.9	42.4
.25	CI Acid Violet 17	.5	1.1	.5	CI Acid Red 14	7.1	37.5
.5	CI Acid Blue 104	.8	1.0	.25	CI Acid Yellow 36	7.2	133.
.25	CI Acid Blue 7	1.1	1.8	.5	CI Acid Blue 25	7.5	133.
.5	CI Acid Yellow 1	1.2	2.8	2.0	CI Acid Red 80	7.7	127.3
.5	CI Acid Green 16	1.3	2.4	.5	CI Acid Black 26A	8.9	21.4
.375	CI Acid Green 3	1.3	3.4	.5	Calcocid Fast Red ASC	9.0	50.0
.5	CI Acid Violet 3	1.3	3.7	1.0	CI Acid Blue 116	9.0	60.0
.375	CI Acid Green 9	1.5	2.4	.5	CI Acid Red 26	9.2	36.6
.5	CI Acid Violet 9	1.6	4.8	.5	CI Acid Red 40	9.4	42.4
.5	CI Acid Violet 29	1.8	6.8	.5	CI Acid Green 25	9.5	136.
.375	CI Acid Yellow 63	1.9	5.2	.5	CI Acid Red 4	10.1	53.6
.375	CI Acid Violet 1	1.9	8.3	.5	CI Acid Red 18	10.8	29.8
.5	CI Acid Blue 59	2.0	9.8	.5	CI Acid Red 1	10.4	45.9
.25	CI Acid Green 50	2.6	6.4	2.0	CI Acid Violet 7	10.9	59.1
.25	CI Acid Green 50	2.6	7.7	.5	CI Acid Green 20	11.8	30.8
.5	CI Acid Red 151	4.3	13.6	.25	CI Direct Yellow 12	12.1	48.7
.5	CI Acid Red 17	4.4	14.6	1.0	CI Acid Black 24	12.1	58.3
.5	CI Acid Red 89	4.6	9.4	.5	CI Acid Yellow 42	12.2	43.8
.5	CI Acid Violet 7	5.0	20.2	.5	CI Acid Orange 10	12.7	164.
.5	CI Acid Orange 54	5.2	22.7	.5	CI Acid Green 25	13.0	164.
.5	CI Acid Blue 45	5.3	85.7	.5	CI Acid Orange 7	13.5	267.
.5	CI Acid Blue 43	5.3	85.7	.375	CI Acid Red 37	13.6	60.8
.5	CI Acid Red 97	5.5	12.9	2.0	Calcocid Fast Red ASC	13.9	55.6
.5	CI Acid Yellow 3	5.7	18.2	.5	CI Acid Yellow 40	14.8	110.
.5	CI Acid Red 88	5.7	23.8	1.0	CI Acid Black 24	15.1	110.
.5	CI Acid Red 151	5.8	44.1	.5	CI Acid Yellow 23	15.1	50.0
.5	CI Acid Red 80	5.9	42.4	.5	CI Acid Yellow 23	16.8	75.0
.25	CI Acid Blue 40	5.9	66.7	.5	CI Acid Green 1	17.9	190.
.5	CI Acid Violet 34	6.0	66.6	2.0	CI Acid Red 40	18.5	160.
.5	CI Acid Orange 8	6.3	30.6	1.0	CI Acid Black 1	19.8	150.
.5	CI Acid Orange 49	6.5	25.9	.25	CI Acid Black 48	20.5	343.
.5	CI Acid Red 66	6.5	65.2	1.0	CI Acid Blue 92	22.1	200.
.5	CI Direct Red 39	6.6	30.0	.5	CI Direct Red 1	24.7	125.
.5	CI Acid Red 73	6.6	46.3	.5	CI Acid Yellow 17	27.9	133.3
.5	CI Acid Blue 78	6.7	85.7	1.0	CI Acid Blue 120	29.6	266.7
.5	CI Acid Blue 45	6.8	75.0	.5	CI Acid Yellow 11	35.3	160.

* Duplicate listings of dyeings at a given concentration are due to dyes of different sales types.

Fade-Ometer exposures (Figure 5). The dyeings were more sensitive to the visible portion of sunlight than to the visible portion of the Fade-Ometer light. This is undoubtedly due to the greater amount of visible radiant energy present in the sunlight.

From the last column in Table I, which lists percent of fading by the ultraviolet portion of sunlight, about two-thirds of values lie above 50%; the average is 56%. A value of 50% fading by ultraviolet light means that by excluding the ultraviolet light the time required for fading will be doubled. The doubled time is equivalent to an increase of one light fastness unit. The percent of fading by the ultraviolet portion of Fade-Ometer light was not calculated, as the meaning is obscure.

Not only are dyes sensitive to light, but many of the fibers also are weakened by exposure to sunlight. After four months' exposure in either Arizona or Florida, the loss in tensile strength of cotton was greatly reduced by screening out the ultraviolet (Table III).

Similarly, the loss in the tensile strength of nylon cloth exposed for two months in Arizona and Florida is lessened appreciably by protecting the nylon from ultraviolet light (Table II). In nylon, however, there appears to be considerable damage caused by visible light or other factors, as shown by the 40–61% drop loss found even behind the ultraviolet absorbing film.

All these data, along with those of other in-

vestigators [1, 4], indicate the desirability of preventing ultraviolet light from reaching dyes and fabrics. One method of protection is by the use of ultraviolet absorbing screens. These screens are usually a clear plastic or varnish containing an ultraviolet light absorber. Current applications for these screens are varnishes for blond furniture, colorless transparent shades for store windows, and clear plastic seat covers. Making safety glass ultraviolet absorbing by putting ultraviolet absorbers in the plastic interlayer of laminated glass is being considered. Because of these great benefits found by the functioning of ultraviolet screens, we have ex-

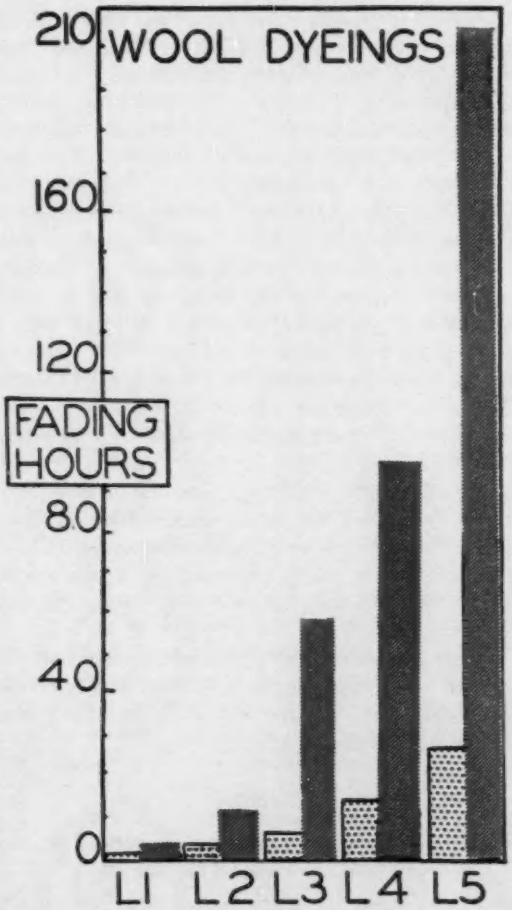


Fig. 4. Fading data of 76 different wool dyeings. The bars showing the average number of Fade-Ometer hours for a 3-Judd color change for dyeings in each light fastness group are dotted for 'not protected' and cross-hatched for 'protected' from ultraviolet light.

TABLE III. Outdoor Exposure of Cotton

Cotton exposed four months	Tensile strength loss, %	
	Florida	Arizona
Behind ultraviolet absorbing film	8	15
Behind untreated film	36	52

TABLE IV. Outdoor Exposure of Nylon

Nylon exposed two months	Tensile strength loss, %	
	Florida	Arizona
Behind ultraviolet absorbing film	40	61
Behind untreated film	85	87

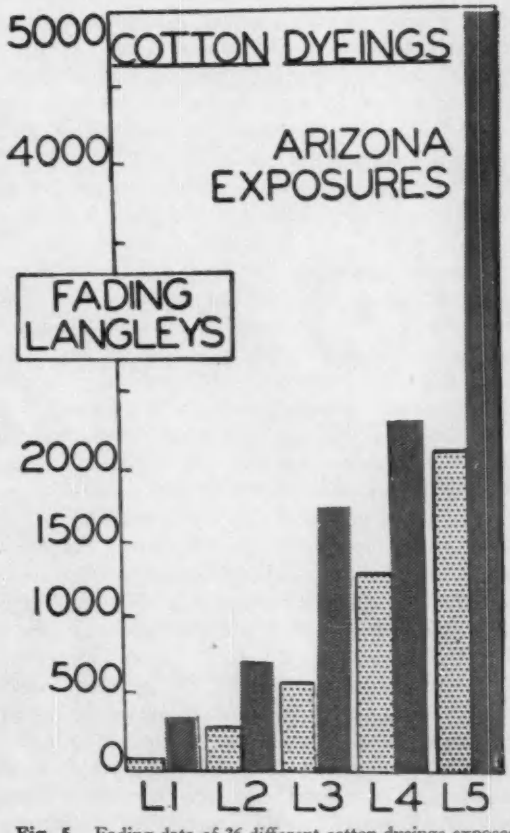


Fig. 5. Fading data of 36 different cotton dyeings exposed in Arizona. The bars showing the average number of Langley units of energy required for a 3-Judd color change for dyeings in each light fastness group are dotted for 'not protected' and cross-hatched for 'protected' from ultraviolet light.

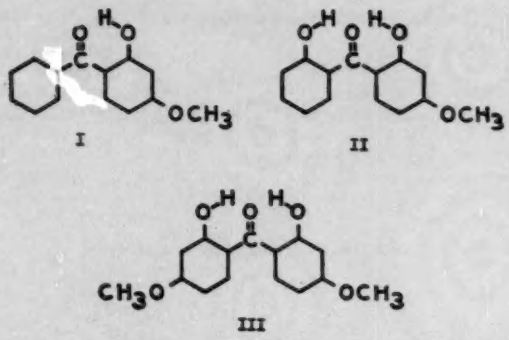


Fig. 6. Structural formulas of three typical ortho-hydroxybenzophenone ultraviolet absorbers.

amined a large number of ultraviolet absorbing chemicals which might be incorporated into screens or directly into materials that are themselves sensitive to ultraviolet.

The usual fate of organic compounds that absorb ultraviolet light is rapid destruction by the ultraviolet radiation. Therefore, chemical compounds which are suitable for use as ultraviolet absorbers must be unique and have these two properties: strong absorption of ultraviolet light and good stability to ultraviolet light. At the present time only one class of organic compounds has been widely tested and been found to have a practical combination of these properties. These compounds, some of which are now available commercially as ultraviolet absorbers, are substituted 2-hydroxybenzophenones. Some of the representative types are shown in Figure 6.

The monohydroxy type (I) is less colored than the 2,2′-dihydroxybenzophenones (II, III). The 2,2′-dihydroxycompounds absorb through a wider range but, in so doing, have a slight yellow color.

The ultraviolet absorbing strength of a compound is best considered for screen purposes as the amount of ultraviolet absorber needed to produce as closely as possible an arbitrary spectrophotometric curve. This arbitrary curve (Figure 2) passes through the 45% transmission point at the 400 mμ wave length. Ideally, there would be some advantage in having less color and more ultraviolet absorption by having the curve pass more steeply through the 45% mark at 400 mμ. In practice, however, the most effective types of ultraviolet absorbers are the 2,2′-dihydroxybenzophenones, which give curves similar to the arbitrary curve. The slight yellow color has little importance in most applications and can be neutralized by adding a trace amount of blue colorant.

It is true that total absence of color is desirable in a few cases, such as in the crystal grade of polystyrene plastics. In such clear plastics, some ultraviolet absorption must be forfeited in order to minimize the absorption of light in the visible range. The mono-2-hydroxybenzophenone type is useful in this case, because its absorption curve in the ultraviolet is shifted to shorter wavelengths by 20 to 30 mμ from the curve shown in Figure 2.

As in all applications of dyes and chemicals, specific applications require that they have specific properties. With ultraviolet absorbers, such properties as higher solubilities can sometimes be obtained by varying the molecular structure. For maximum effectiveness of ultraviolet absorbers, complete dispersion or solution is necessary. Also, the compound must remain unchanged during application and processing in order to maintain its spectral absorption characteristics and its original light stability. This means it must be resistant to heat and reagents. It is interesting to note that the 2-hydroxybenzophenone class, in general, measures up very well in regard to these specifications.

At the present time, ultraviolet absorbers are finding their greatest use in protecting plastics from ultraviolet degradation. In such applications only a small amount of absorber is necessary for this protection. In exposure tests in Florida, for example, 0.25% of 2-hydroxy-4-methoxybenzophenone has been found to retard the yellowing of clear polyester resin by a factor of ten.

The resistance of polyvinyl plastics to sunlight is greatly improved by adding ultraviolet absorbers. The 2,2′-dihydroxy-4-methoxybenzophenone (II) is particularly effective in delaying the formation of brown spots in polyvinyl chloride during outdoor exposure.

Other plastics are also protected by ultraviolet absorbers. For example, the yellowing of polystyrene is slowed down, and the embrittlement of cellulose acetate films is greatly delayed.

Textiles

The application of ultraviolet absorbers to textiles has not yet been explored very thoroughly. The ultraviolet absorbers which have been evaluated are not substantive to cotton. However, some of the ultraviolet absorbers can be dyed onto wool and onto the synthetic fibers such as acrylics, cellulose acetate, polyamides, polyesters, and others. The ultraviolet

absorbers are probably distributed throughout most of these hydrophobic fibers essentially as in a solid solution. As a preliminary experiment, we have added 4% on the weight of cellulose acetate fiber of 2,2'-dihydroxy-4-methoxybenzophenone in the form of an emulsion directly to the dye bath in the dyeings of eight colorants on cellulose acetate. About 75% of the absorber exhausted onto the fiber in this case, although higher exhaustions have been obtained. In many of the cases, there was a slight shift of shade because of the high concentration and slight self color of the ultraviolet absorber. The beneficial effect of this ultraviolet absorber on the light fastness of these dyed fabrics is described in Table IV. Most of the names in this table are the new color index names. The average improvement is 60%.

In addition to protecting dyes, the treatment of certain fibers can also be beneficial to the fibers. Exposure of nylon in the sunlight has already been shown to result in reduced tensile strengths. Application of 1% of 2,2'-dihydroxy-4-methoxybenzophenone has retarded some of this sunlight effect (Table V). Because this absorber gives a slight yellow cast to such fibers as nylon, it presents a problem in some textile applications.

Another approach is to incorporate the ultraviolet absorber into a textile resin and apply the mixture to the fabrics. We are presently investigating certain aspects of this method. The problems that have evolved in this area are concerned with the thinness and continuity of the coated films as well as the rather high concentrations of ultraviolet absorber necessary for effective screening of the ultraviolet light.

The ultraviolet light is an important cause in the fading of practically all dyes, in the weakening of fibers and fabrics, and in the photodegradation of many other substances. Ultraviolet absorbers have been applied to many substances and have been successful in many cases in neutralizing the destructive attack of ultraviolet light. However, many more studies on their application to fibers will be necessary before maximum effectiveness can be attained.

TABLE IV. Dyeings of Cellulose Acetate Tricot

	Fade-Ometer hours to fade 3 Judds		Improvement, %
	Untreated	Treated*	
1% "Yellow MG"	7	13	86
1% Disperse Yellow 3	10	15	50
1% Disperse Orange 3	23	41	78
1% Disperse Orange 7	26	43	65
1% Disperse Red 1	50	86	72
1% Disperse Blue 3	71	118	66
4% Disperse Black 9	79	109	38
1% Disperse Violet 1	102	126	24

* Treated to contain 3% 2,2'-dihydroxy-4-methoxybenzophenone.

TABLE V. Effect of Ultraviolet Absorber on Sun Exposure of Nylon

Nylon after two months	Tensile strength loss, %	
	Florida	Arizona
Untreated	96	89
Treated with 1% 2,2'-dihydroxy-4-methoxybenzophenone	78	78

Acknowledgment

The authors wish to acknowledge the assistance in gathering data for this paper of the staffs of the Chemicals and Intermediates Research Section of the Research Division and of the Dyes Application Laboratory of the Organic Chemicals Division. We wish particularly to mention the help of Dr. W. B. Hardy, J. L. Rodgers, L. G. Mattei, A. F. Klein, F. Vossel, and L. Manara. We are also grateful for the permission received to use data from the files of the Research Division of the American Cyanamid Company.

Notice

Nothing contained herein shall be construed to imply the nonexistence of any relevant patents nor to constitute a permission, inducement, or recommendation to practice any invention covered by any patent owned by American Cyanamid or others, without authority from the owner of the patent.

Literature Cited

1. Gantz and Sumner, TEXTILE RESEARCH JOURNAL 27, 244 (1957).
2. Hardy and Coleman, "Proceedings of the Perkin Centennial," 69–75 (1956).
3. Judd, "Color in Business, Science and Industry," New York, Wiley, 256, 269 (1952).
4. McLaren, *J. Soc. Dyers Colourists* 72, 86 (1956).

Whither Rayon?[1]

John Wharton and G. V. Lund

Courtaulds, Inc., Mobile, Alabama

Abstract

A general review of certain developments in the viscose rayon production industry is given, together with some account of how rayon can be used in the wash and wear field.

SINCE man-made fibers were first produced from cellulose by Cross and Bevan in 1904, major developments have resulted in the use of rayon for a wide variety of end products, so that in one form or another, upwards of 1 billion pounds per year of rayon are used in the U.S. alone. In recent years there has, of course, been competition from the so-called synthetic fibers. Improved know-how in the aftertreatment of cotton fabrics has also provided a stimulus and challenge to the viscose rayon industry, so that development of new types of rayon fibers has been rapid, and we may expect a considerable commercial exploitation of some of these materials within the next year or two. We believe that the rayon industry is a growing one and that increasing production of man-made fibers based on cellulose to a level of 2 to 3 billion pounds a year in 1970 to 1975, within the U.S. alone, is not improbable.

The so-called regular rayon in continuous filament or in staple form has dry filament tenacities of 2.2–2.6 g./den. with 17–25% elongation at break. These fibers have lower tenacities but higher elongation when wet. The fibers show a highly orientated skin, and the water imbibition as defined by the perceatage of water on bone-dry cellulose which is retained after wetting and centrifuging under forces of 1000 G for 5 min. is about 100–120%. About 85% of all the so-called regular viscose staple fiber produced today receives afterfinishing treatments in fabric form.

Following the production of regular viscose staple fiber, the first strong viscose staple fiber was produced in quantity just before World War II, where by alterations to the viscose, spinning bath, and stretch conditions, the skin thickness of the filament was greatly increased and high orientation of the crystalline or micellar structure was possible. With this type fiber, tenacities up to 3.5 g./den. and elongations around 20% in the dry state are usual, while wet tenacities may be as high as 1.8–2.3 g./den. The water imbibition of the fiber is still high at 80–100%.

Some success has been achieved using a strong viscose staple in the production of fine count yarns, both for 100% rayon yarns and in cotton–rayon blends. In Europe, strong viscose staple is also being used for many industrial purposes, more especially where a high work of rupture in the dry state is desirable.

Between 1938 and 1948 the use of cotton in automobile tires was quietly but completely eliminated by the use of continuous viscose rayon tire yarns, which showed far less heat degradation and exhibited a very much higher work of rupture (shock resistance) than any type of tire cord which was made from cotton. The early viscose continuous filament tire yarns showed skin–core fiber structure very similar to that present in the so-called strong viscose staple fibers.

Since 1948, very rapid advances have been made in improving the properties of viscose tire yarns to meet the threat offered by nylon. Whereas in 1952 conventional viscose tire cord with a strength of 25 lb. was considered good, recent super-super viscose yarns give cord strengths close to 40 lb., and still further increases in strength for a given weight of fiber are possible. Resistance to fatigue on repeated flexing of the yarns imbedded in rubber has also been improved 100–200%. The quantity of the super-super viscose fibers which has found its way into commercial usage is still small, but during the coming year they will be produced in adequate bulk to have an important stabilizing effect in the automobile tire production field. The super viscose

[1] Presented at the 28th Annual Meeting of the Textile Research Institute, New York City, March 14, 1958.

fibers show relatively homogeneous cross sections free from obvious skin and core differences; the work to rupture in the dry state, as may be seen in Figure 1, is very high indeed.

As might be expected, the know-how accumulated in the production of tire yarns has been used to make special viscose staple fiber products represented by duPont's 109, AVC's XL, and Courtaulds Limited's M-95. In the near future we may well see the use of these so-called super viscose fibers not only replace strong viscose staple but also make some inroads into the dominant position held by cotton where certain industrial uses are concerned. The price of these fibers is very attractive compared with that of such synthetics as Nylon 66. In the dry state the viscose super fibers certainly offer the best buy per pound of strength available.

While it has not been found necessary to make the super viscose staple fibers so strong as those now being introduced for tire yarns, tenacities of 4 g./den. dry and 3 g./den. wet can be obtained without great difficulty. The fibers have water imbibitions of 70–75%; abrasion resistance is very high. To achieve crease resistance and full dimensional stability in fabrics made from super viscose staple fibers, however, afterfinishing treatments are necessary, and these unfortunately tend to reduce the very high abrasion resistance and the high work of rupture, so that compared with the very bright prospects for these fibers in industrial fields, the more normal types of viscose staple may offer a better buy in the apparel field.

Another type of viscose staple which was first made in Japan just before World War II under the name of Toramomen is interesting, since it is said to show more cotton-like characteristics than any of the rayons already discussed. This interesting material has a high tenacity but a very low elongation, wet and dry, so that the work of rupture is not higher than that of cotton. The Toramomen type fibers are highly crystalline; this high crystallinity leads to a low fiber compliance, with resulting firmness of hand in fabrics.

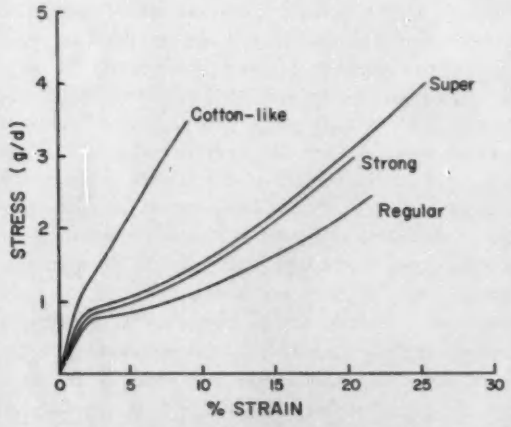


Fig. 1. Rayon stress–strain curves at 65% RH.

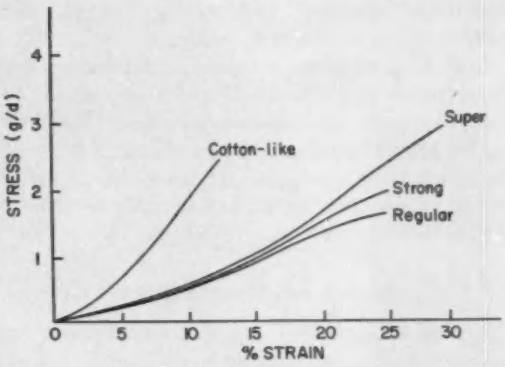


Fig. 2. Wet rayon stress–strain curves.

The wide variety of properties available in various viscose staple fibers today, as distinct from what was recognized 10–20 years ago, may be seen in Figures 1 and 2.

Crimp Staple

By special modifications of viscose and spinning bath composition, it is possible to produce viscose fibers in various deniers and staples which have a natural crimp. Sisson and others have shown that this crimp is due to irregular skin formation around the filaments; i.e., the skin is thick on one side and thin on the other. In general, the number of crimps per inch decrease and the crimp amplitude increases as the filament denier rises. Crimped viscose staple fiber in 8 and 15 den. has been used for carpet production for some years now; provided an adequate weight of rayon is used for a given area, excellent results can be obtained. Recent research has given some promise that crimp retention and the recrimping energy of the fiber after processing may be increased for the finer rayon deniers, so that lofty and bulky fabrics result. In knitwear the effect of crimp in present 3-den. viscose rayons is well apparent, but in woven fabrics the effect is marginal.

For tufted materials, such as chenilles and bedspreads, crimp is always desirable.

In Britain, which has a reputation for fine woolens, rather more than 50 million pounds of viscose fiber each year goes into blends with wool. Many fine quality fabrics containing 70% wool and 30% viscose staple are being produced; the use of viscose staple in limited amounts enables higher grade wools to be used without increase in overall costs.

Spun Dyed Viscose Fibers

By incorporation of special pigments into the viscose spinning solution, it is possible to produce colored viscose fibers which have exceptional resistance to light and chemical degradation. In fact, it may be said that many of the pigments are more stable than cellulose itself. Our company produces 26 different colored spun dyed staple fiber products in various deniers and staples. Of these, 17 have a light fastness equivalent to a 500-hr. rating in Florida sunshine, while all of the remainder have better fastness than can be obtained in the same color by conventional dyeing.

With the use of Coloray staple fiber, a large number of shades and colors can be made by blending, as from a paint box, with relatively few basic colors. The cost of Coloray is always much lower than the cost of fiber dyed by vat dyes, which are the only type of dyes approaching the light fastness of the pigments used. As was pointed out by John Boulton on a recent visit to the States, the rather expensive use of heat and power which is usual to conventional dyeing is also eliminated.

For many garments or fabrics which have been treated so as to survive frequent washing, satisfactory dyeing has always been a problem, since after many washings, due to the effect of alkali, chlorine, or just physical loss of dye, the garments may have a washed-out appearance. These adverse effects cannot occur with Coloray, so that its use is ideal for material and garments which are given wash and wear finishes.

It has always been recognized that one disadvantage of normal viscose rayon fibers, for many purposes, is their capacity to swell when wet, more especially in the transverse direction. Pilot plant products have been made by Courtaulds, Inc. Research which show a swelling in water no greater than that normally shown by unmercerized cotton. The resistance to alkaline treatments has also been greatly increased. Evaluation of these fibers for various end uses is in progress.

The Southern Regional Research Laboratories, in association with Rohm and Haas, have done excellent work towards wash and wear finishes on cotton. Recently it has been possible to give rayon fabrics, of suitable construction, wash and wear finishes which are as satisfactory as any of those normally applied to cotton.

In general these finishes consist of amino resins in association with hand builders and silicone compounds which are all dissolved or emulsified in water to an adequate concentration.

If the material or garment has been soaked in the appropriate mixture and excess liquor has been squeezed or centrifuged out, it can be dried and cured either in one operation or by drying first and curing later to produce wash and wear effects which are stable to many launderings. It is important that the wash water for laundering the treated garments should not be acid (below pH 7) and that the temperature of washing should not exceed 140° F.; these requirements also apply to wash and wear cotton material or garments. Aftertreatments cause a reduction in fiber extensibility to 10% or below; the water imbibition of the fiber is usually down to 35% or below. The fiber elastic recovery, as determined by a short term recovery from 3% extension, rises from about 35% in the untreated fibers up to 65% or even higher. All these changes in the fiber may be associated with the cross-linking effects of the amino resin. The dependence of these effects on resin concentration is shown in Figures 3 and 4 and Table I.

Owing to the rather amorphous nature of regular viscose fibers, a considerably higher percentage of resin is necessary to produce good effects as compared to what is usual for cotton afterfinishing treatments. At the same time, this is not without advantage, since the tear strength and general ballistic properties of the treated rayon fabrics are superior to those of cotton. It has been known for some time that modification of cotton by caustic soda treatment or by liquors containing zinc chloride gives an improved fiber for resin treatment, to avoid low tear strengths. Normal rayon, being more amorphous than cotton, does not require any preswelling treatment, and there is accumulating evidence to show that the use of rayon in blends with cotton may be very desirable, where afterfinish treatments are given,

to reduce the well known lowering of tensile properties which occurs on the treatment of cotton alone.

It has been observed that the effects of chlorine retention on resin treated rayon/cotton blends is markedly less than that of resin treated 100% cotton, since at high ironing temperatures the effect of traces of acid is much less serious on rayon.

For crease resistance and wash and wear treatments, the quality of the final goods is always in the hands of the finisher. To achieve the necessary basic changes in the fiber with the use of the special finishes required, proper concentrations, pH, and curing conditions must be used to give optimum results. Under proper conditions of treatment, the low water imbibition, high fiber elastic recovery, and the lower extension of the fibers are retained when the material is subjected to quite severe alkaline washing conditions. We must again stress, however, that truly wash and wear finishes on cellulosic fibers for both rayon and cotton will give fully satisfactory results only if the garments are washed at 140–150° F. or less. It is also important to see that the wash waters used are not acid. However, this is not normally a problem, since most city water is alkaline to avoid pipe line corrosion.

The synthetics have no advantage so far as temperature effects are concerned, since at any elevated temperatures a marked increase in the compliance of these fibers occurs, so that distortion and shrinkage can follow, especially under low washing loads. In fact, the synthetic fibers in fabric form are very sensitive to high drying temperatures in the tumble drier, while wash and wear viscose rayon and cotton fabrics may be dried at temperatures well above 180° F. with success.

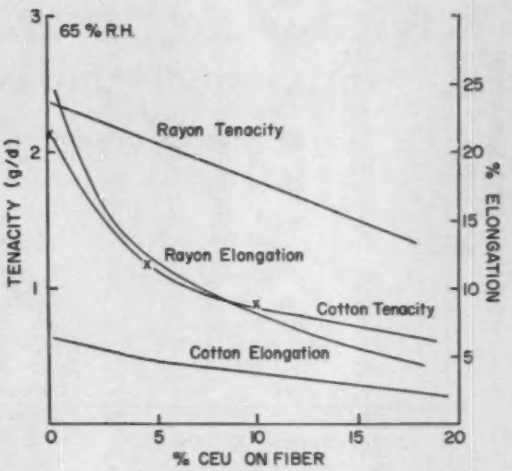


Fig. 3. Dependence of fiber tenacity and elongation on resin concentration.

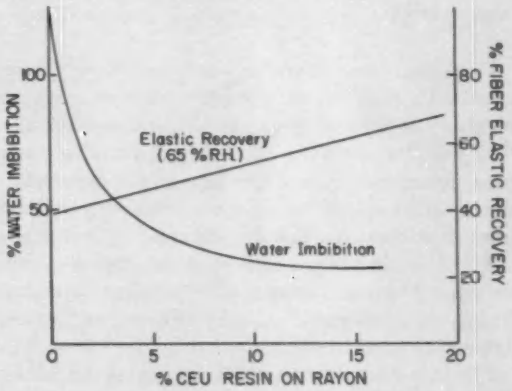


Fig. 4. Dependence of water imbibition and elastic recovery on resin concentration.

TABLE I

Sample	% CEU soln.	Fiber dry tenacity, g./den.*	% Dry elong.*	% W.I.	% Fiber elastic recovery
Rayon	Control	2.26	22.5	118	36
Rayon	5	2.03	11.8	39	52
Rayon	10	1.71	7.0	33	57
Rayon	15	1.42	4.3	29	63
Rayon	20	1.27	4.7	28	68
Cotton	Control	2.10	6.0	45	46
Cotton	5	1.15	4.5	26	62
Cotton	10	.90	3.1	22	60
Cotton	15	.82	4.0	20	broke in test
Cotton	20	.52	2.2	16	broke in test

* Single fiber properties obtained on an Instron machine with 1-in. gauge length and 100% extension per minute. Cotton data corrected for 0.5 in. gauge length. Cotton sample was American Upland middling, 1¼-in. staple length.

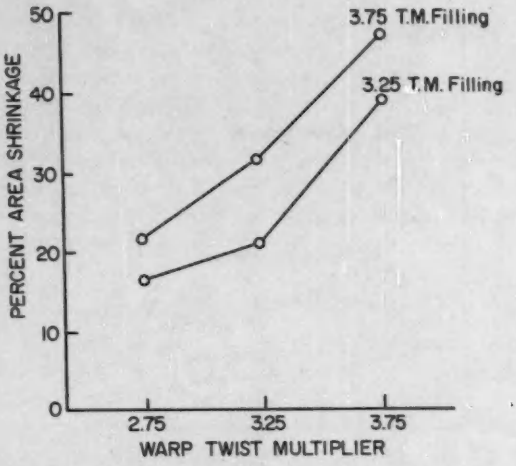


Fig. 5. Dependence of fabric area shrinkage on yarn twist (40 washes at 1-lb. load); regular rayon, 20's yarn, 60 × 40 fabric, 1½ × 1⅝ in. staple. Shrinkage includes desizing shrinkage.

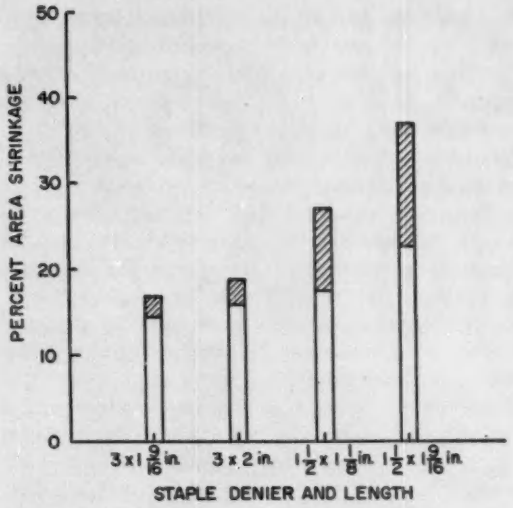


Fig. 6. Effect of denier and staple length upon fabric laundering shrinkage at constant yarn twist and fabric construction. Griege construction: 20/1 warp + filling, 60 × 40. Hatched area: felting shrinkage. Shrinkage includes desizing shrinkage plus ten washings.

It is clear that fibers in wash and wear fabrics must have high elastic recovery together with an adequate amount of strength. However, it is also clear that the possession of these properties by fibers does not necessarily result in fabrics with good wash and wear characteristics; the effects of yarn and fabric construction are also important.

The twist in the yarns from which rayon fabrics are made has a very marked effect on the shrinkage during the laundering of untreated rayon fabrics; this is illustrated by Figure 5.

The importance of this is the stability of the fabrics after a very large number of launderings, during which any resin will hydrolyze. This is also important to blends of cotton and rayon which are not to be given resin finishes. It is clear that the twist in the yarns made from blends of cotton and rayon must be lower than that in the all cotton fabrics if satisfactory stability to a large number of launderings is to be obtained. Fortunately, this is also desirable from the point of view of yarn strength.

Fiber denier also has a marked effect on fabric stability (Figure 6), coarser denier fibers giving much more stable fabrics. Since 3-den. fibers give fabrics which need far less "hand building" than similar fabrics made from 1½-den. fibers, it is clear that wherever the yarn count will permit, 3-den. fibers should be used in wash and wear rayon fabrics. This effect is also most marked in knitwear. Although knitted fabrics made from 1½-den. have unsatisfactory stability to laundering, knitted fabrics made from 3-den. rayon staple are of comparable stability to similar fabrics made from cotton.

It may be wondered why this paper has been called "Whither Rayon?". While rayon producers have always been cautious about overstating the position, it has been possible to produce fibers from cellulose with a very wide variety of properties ranging from cotton-like to those with works of rupture equal to nylon. The basic structure of regenerated cellulose, both chemically and physically, allows many variations to be made; in truth, 57 varieties—if 57 varieties could profitably be used.

While rayon is regarded as one of the older and less glamorous fibers, very great progress has been made in the art of manufacturing fibers from cellulose. A proper determination of what is desirable in a fiber for a given end use in all that is necessary to enable further substantial advances to be made.

On the Physical Properties of Rayon and Nylon 66 Tire Cords at Elevated Temperature[1]

Frank R. Charles and Clement Tarzi

Industrial Cellulose Research Ltd., Hawkesbury, Ontario, Canada

Abstract

Currently produced rayon and nylon tire yarns, greige cords, and dipped cords (the nylon dipped cord having been Kidde treated, hot-stretched, and heat-set) were tested for reversible physical properties at 70°, 100°, 220°, and 300° F. As the temperature was raised, the nylon samples showed greater loss of breaking strength, greater increase in extensibility, greater loss of Hookean slope, and (for the cords) greater increase in contracting force than the corresponding rayon samples. Heat aging at 220° F. in an air-circulating oven for periods up to five days caused no significant change in the values obtained at 220° F. for strength, extensibility, or Hookean slope for either the rayon or nylon samples.

The rayon cords had the expected advantage of a high initial modulus; this advantage over the nylon cords was improved as the testing temperature was increased from 70°–300° F. It is believed that this would mean less growth and a smaller degree of cyclic extension, for tires made from the rayon cords, under temperature conditions likely to be met with in normal driving.

Introduction

It is well known today that automobile and truck tires heat up to high temperatures in service. It is known that tire temperatures of 220° F. and above are occurring frequently, and that prolonged fast driving in very hot weather will raise tire temperatures up to as high as 300° F. Data supporting this were presented by Hershey [4] at the SAE symposium last June.

It is most important to know, therefore, the effect of such high temperatures on the physical properties of the textile cords commonly used for tire reinforcement.

The two textiles used in volume today for automobile and truck tires are rayon and nylon 66.

Wood and Kilby [9] studied the effect of elevated temperature on the extensibility and creep of rayon and nylon tire cords and found definite advantages for rayon.

Illingworth and Kilby [5, 6] clearly differentiated between the reversible strength loss due to plastic flow at elevated temperature and the slow permanent loss of strength that takes place with time, closely associated with oxidation, which can be inhibited to a large extent in both rayon and nylon by suitable finish treatments [3, 5].

Illingworth and Kilby [6] pointed out that since moisture diffuses more rapidly through rubber when hot, there is a greater tendency for moisture to leave the fabric than for the converse effect when the tire is standing at normal temperature (in which case, according to Gardner [1], 4–5% moisture slowly rediffuses into the cords of a rayon tire). The properties of the fabric in the hot, bone-dry state are consequently of greater importance than those in the normal conditioned state.

They developed a hot box attachment for the Scott IP-4 tester, fed with predried air, such that the predried yarn or cord was totally enclosed during the test at elevated temperature and thus was tested in the hot, completely bone-dry state.

Illingworth and Kilby's data showed greater reversible strength loss for nylon than rayon cord at elevated temperature. The values in Table I have been calculated from their curves.

Goy [2], in a general article on textile control in tire production, quoted values from Illingworth and Kilby [6] which again showed nylon to be less heat stable at the higher temperatures than rayon, but with a smaller difference than above.

Specklin [8] quoted comparative tests by the

[1] Presented at the 28th Annual Meeting of the Textile Research Institute, New York City, March 13, 1958.

U. S. Aeronautical Research Laboratory (1953) on rayon and nylon singles yarns at high temperature (after 24 hr. at the same temperature) which can be expressed as follows:

	Viscose H.T.	Nylon 70 den.
68° F.	100 (2.4 g./den.)	100 (4.2 g./den.)
212° F.	96	79
347° F.	79	48

Mallory [7] reported at the 27th Textile Research Institute Annual Meeting last March that "nylon and to some extent rayon exhibit decreased modulus at high temperature and load. They also show contracting forces with rising temperature."

Present Investigations

The present studies were prompted by the lack of published data on the effect of elevated temperature on rayon and nylon dipped cords, i.e., in the state in which the cords actually enter the tire.

Rayon and nylon tire yarns, greige cords, and

TABLE I. Tests in the Completely Bone-Dry State

Temp., ° F.	Rayon cord 1180/3	Rayon cord 1650/2	Nylon cord 210/4/2
	Breaking strength		
68	100 (2.36 g./den.)	100 (2.73 g./den.)	100 (6.58 g./den.)
140	92	92	84
212	85	82	72
248	82	79	65
284	79	76	61
	Extensibility		
68	100 (16.8%)	100 (9.8%)	
140	104	106	
212	115	118	No data given
248	120	120	
284	130	123	

TABLE II. Tests on Scott Inclined Plane IP-4 Tester

		Rayon			Nylon		
		Singles	Greige cord	Dipped cord	Singles	Greige cord	Dipped hot-stretched heat-set cord
Denier		1665	4010	3820*	940	2071	1830*
# Filaments		720	1440	1440	140	280	280
Twist Z/S—t.p.i. nominal		0	12.0/12.6	12.0/12.6	1.0		11.8/12.8
Twist Z/S—t.p.i. actual		0†	12.2/12.4	12.2/12.4	0.7†	13.2/13.6	12.2/12.5
Moisture content, %		12.0	12.0	5.5	3.8	3.8	2.5
Breaking strength, Kg.	O.D.	9.30	15.04	14.40	7.46	13.60	13.56
Breaking strength, Kg.	Cond.	7.95	12.90	12.75	7.44	13.17	13.08
Breaking strength, lb.	O.D.	20.5	33.2	31.7	16.5	30.0	29.9
Breaking strength, lb.	Cond.	17.5	28.4	28.1	16.4	29.0	28.8
Tenacity, g./den.	O.D.	5.58	3.77	3.77	7.94	6.57	7.41
Tenacity, g./den.	Cond.	4.77	3.22	3.34	7.92	6.36	7.15
Extensibility at break, %	O.D.	9.9	14.0	12.9	20.1	29.8	21.3
Extensibility at break, %	Cond.	13.4	20.3	19.2	16.8	27.3	19.9
Extensibility at 10 lb., %	O.D.	2.0	3.0	2.5	13.0	13.5	9.0
Extensibility at 10 lb., %	Cond.	6.0	7.0	6.0	10.0	13.0	8.0

* Denier of dipped cord less percent latex solids.

† Twisted to 3.4 Z t.p.i. prior to all treatments and tests. Tests were carried out at a loading rate of 18 g./den./min.; atmosphere—57.5% R.H., 70° F. dry bulb.

dipped cords, representative of today's qualities actually going into Canadian tires, were purchased on the open market in the spring of 1957 as follows:

	Super Super Rayon	
Singles yarn	1650/720	
Greige cord	1650/720/2	
Dipped cord	1650/720/2	Kidde treated, 5% RFL solids pick-up

	Nylon 66	
Singles yarn	840/140	
Greige cord	840/140/2	
Dipped cord	840/140/2	Kidde treated, hot-stretched, and heat-set, 3% RFL solids pick-up.

The normal physical tests on these samples using the Scott IP-4 inclined plane tester are given in Table II, together with twist measurements and moisture determinations.

It can be seen from the values obtained that the yarns and cords purchased were reasonably representative of their grades.

Four points in the range of tire operating temperatures were selected for study—70°, 100°, 220°, and 300° F.

The various samples were tested at these temperatures in equilibrium with the conditioned air of the testing room (57.5% R.H. at 70° F.), raised to the testing temperature.

The Instron tester was used for this study because of its greater precision than the inclined plane type.

The Kidde treated hot-stretched and heat-set nylon cord sample is referred to hereinafter for simplicity as the nylon dipped cord.

Experimental

Heating Device

A heating box was designed to surround the entire length of the thread under test including the jaws of the tester. Roseville spool type jaws were adapted to the instrument. A lengthened upper jaw rod was used in order to permit the required travel of the descending heating box during the extension.

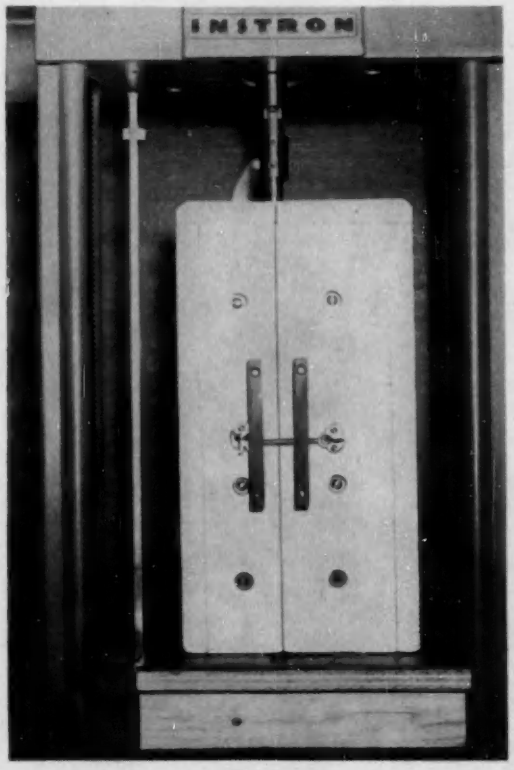


Fig. 1

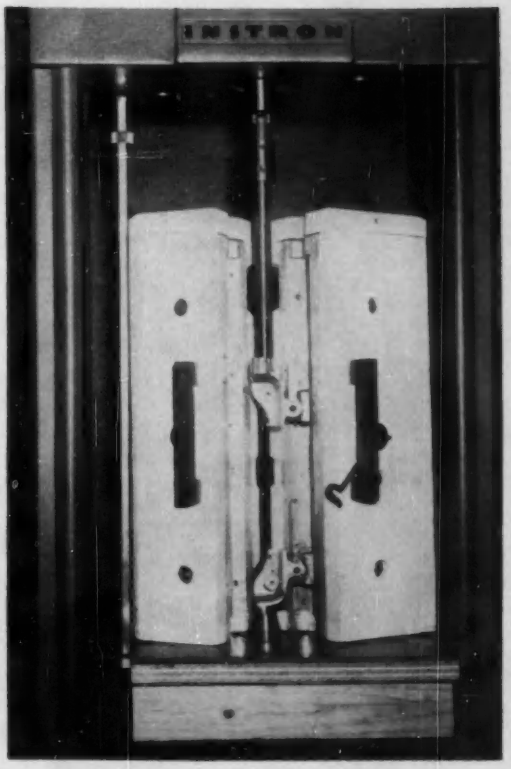


Fig. 2

The general design of the box can be seen from the photographs, Figures 1 and 2, and the sketch, Figure 3. It consisted of two insulated cast aluminum blocks, hinged together at the back and resting on a base fitted on the cross-head of the Instron. Heating was effected through four 150-watt cartridge type heaters spaced within the blocks to give a uniform temperature. A thermocouple was used to measure the temperature at various locations along the thread, and an accuracy of ± 5° F. was maintained.

Technique

The heating box was closed and adjusted to the testing temperature. The box was then opened, the yarn or cord to be tested clamped between the jaws without tension, and the box closed again.

The sample was allowed to attain equilibrium with the surrounding atmosphere (10 min.). Restricted convection carried out excess moisture through the $\frac{1}{16}$-in. clearance around the top clamp rod. The load–elongation curve was then drawn using the following conditions:

Length of specimen between jaws	10 in.
Extension rate	50%/min.
Chart speed, in./min.	10
Cross-head speed, in./min.	5
Extension magnification	2
Load selector—initial (for Hookean slope)	0–4.54 Kg. full scale
Load selector—final (for break)	0–22.70 Kg. full scale

Results

Reversible Effect

Results obtained are given in Table III. All values were determnied from the stress–strain curves given by the Instron tester. Each figure in the table is the average of 10 individual tests.

Breaking strength and extensibility are shown graphically in Figures 4 and 5.

Hookean slope was determined as the slope of the initial straight line portion of the force–extension

TABLE III. Tensile Tests on Instron Tester at 100°, 220°, and 300° F.

(in equilibrium with standard atmosphere (57.5% R.H./70° F.) at the test temperature)

		Rayon				Nylon			
	Temp., ° F.	Breaking strength, Kg.	Breaking extensibility, %	Hookean slope, Kg./%	Contracting force, Kg.	Breaking strength, Kg.	Breaking extensibility, %	Hookean slope, Kg./%	Contracting force, Kg.
Singles	70	6.97	12.7	1.65	—	6.56	17.2	0.38	—
	100	6.68	10.2	1.60	—	5.78	16.7	0.30	—
	220	6.15	9.6	1.57	0.15	3.91	23.5	0.16	0.30
	300	5.61	9.2	1.62	0.28	3.02	24.4	0.16	0.34
Greige cord	70	11.41	17.3	0.99	—	12.23	26.7	0.34	—
	100	10.75	13.7	0.88	—	9.55	28.1	0.25	—
	220	10.42	14.0	0.86	0.026	7.42	31.6	0.19	0.29
	300	8.93	13.6	0.70	0.018	6.16	32.7	0.18	0.35
Dipped cord	70	12.08	19.1	1.32	—	12.30	19.2	0.57	—
	100	11.64	15.7	0.98	—	9.87	19.6	0.30	—
	220	9.16	14.3	0.98	0.031	8.27	19.9	0.25	0.17
	300	7.83	13.5	0.84	0.045	6.56	21.1	0.25	0.36

TABLE IV. Percent Strength Retained

	Rayon			Nylon		
	Singles	Greige cord	Dipped cord	Singles	Greige cord	Dipped cord
Initial value—Kg.	6.97	11.4	12.0	6.56	12.2	12.3
100° F.	96	94	96	88	78	80
220° F.	88	91	76	60	61	67
300° F.	81	78	65	46	50	53

curve, from the initial magnified portion of the Instron curve. It is shown graphically in Figure 6.

The contracting force developed on attaining the test temperature during the short heating period was determined from the Instron chart and is plotted against temperature in Figure 7.

To illustrate the data given in the tables and curves, Figure 7A shows typical load–extensibility curves for the dipped cords at the various temperatures.

Breaking strength (*Figure 4*). The rayon samples showed considerably less loss of strength than the nylon samples as the temperature of testing was raised. The percentage of strength retained is given in Table IV.

Although the nylon greige and dipped cords started with slightly higher conditioned breaking load than the rayon samples, the 220° F. values were only 71% and 90% respectively of the corresponding rayon cords, and the 300° F. values only 69% and 84%.

Extensibility (*Figure 5*). The extensibility of the nylon singles and greige cords increased considerably with temperature due to the thermoplastic nature of the fiber. The dipped nylon cord showed

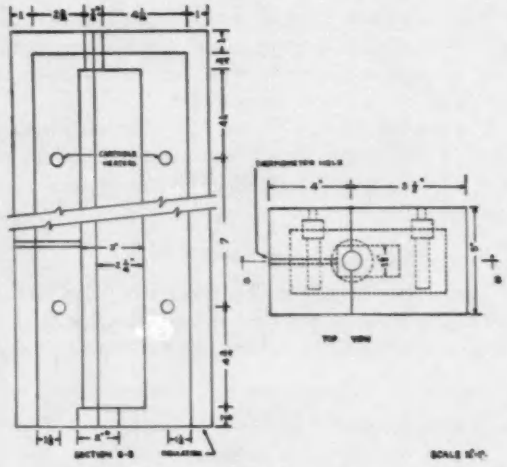


Fig. 3

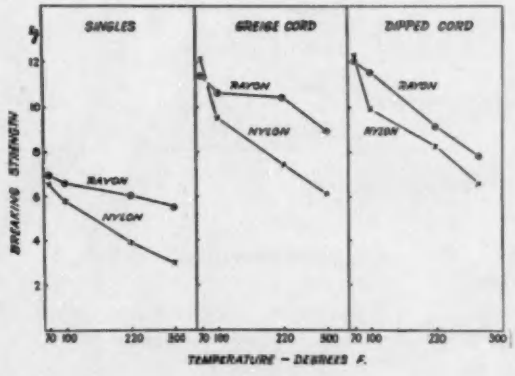


Fig. 4

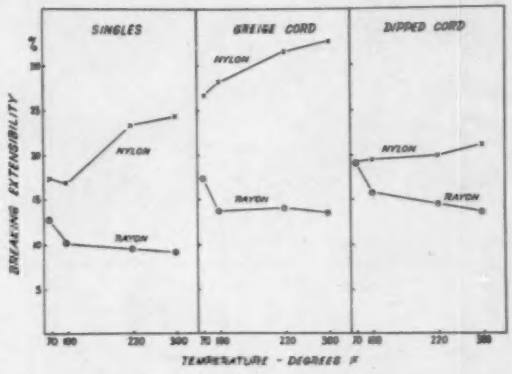


Fig. 5

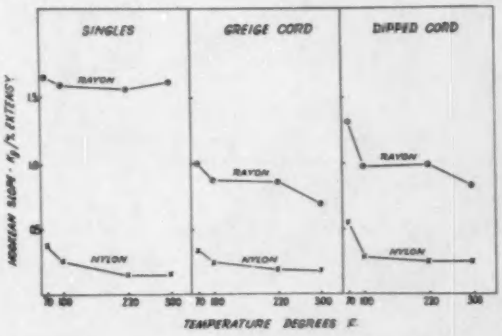


Fig. 6

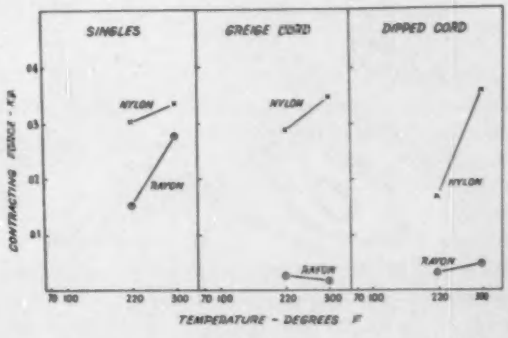


Fig. 7

a smaller but still a definite increase of extensibility with temperature.

The rayon samples showed a decreased extensibility at 100° F., and above this temperature either no change or a small decrease. At 220° F. the nylon greige and dipped extensibilities were 2.3 and 1.4 times those of the corresponding rayon samples, and at 300° F. the ratios were respectively 2.4 and 1.6.

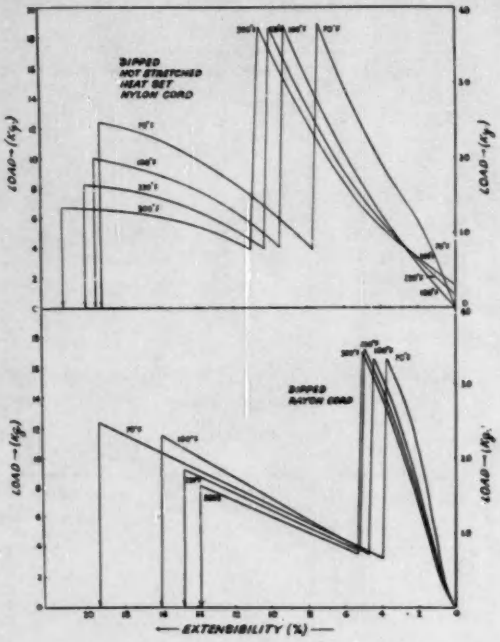


Fig. 7A

Hookean slope (initial modulus) (*Figure 6*). In addition to having a considerably lower Hookean slope than the rayon samples, the nylon samples also exhibited greater loss as the temperature was raised. The percentage figures are tabulated in Table V.

Although hot-stretching and heat-setting had improved the Hookean slope of the dipped nylon cord over the greige cord value, the dipped cord value at ordinary temperature was still only 44% that of the dipped rayon cord, and at 220° F. it had fallen to only 26% that of the dipped rayon cord.

For those who are more familiar with the characterization of tire cords by the extensibility at low loads (5 and 10 lb.), Table VI shows the values obtained for the dipped cords at the various temperatures.

The important point to notice is that, at both 5- and 10-lb. load, the elongations of the rayon cords even at high temperature were still below those of the nylon cords at low temperature.

Contracting force (*Figure 7*). The contracting force of the nylon dipped cord reached 360 g. at 300° F. compared to only 45 g. for the rayon dipped cord.

Typical Force–Extension Curves

The curves of Figure 7A show very clearly the great differences between the rayon and nylon dipped cords with regard to Hookean slope and extensibility

TABLE V. Percent Hookean Slope Retained

	Rayon			Nylon		
	Singles	Greige cord	Dipped cord	Singles	Greige cord	Dipped cord
Initial value—Kg./%	1.65	0.99	1.32	0.38	0.34	0.57
100° F.	97	89	74	79	74	52
220° F.	95	87	75	43	55	44
300° F.	98	71	63	44	53	44

TABLE VI. Percent Extensibility at Various Loads

	Rayon			Nylon		
	Dipped cord			Kidde-treated, hot-stretched, heat-set cord		
Temp., ° F.	5 lb.	10 lb.	Break	5 lb.	10 lb.	Break
70	1.8	6.5	19.1	4.7	8.0	19.2
100	2.6	6.7	15.7	6.5	9.6	19.6
220	2.5	6.8	14.3	7.1	10.4	19.9
300	3.0	7.7	13.5	7.2	11.6	21.1

TABLE VII. Tensile Tests at 220° F. After Various Periods at This Temperature

(in equilibrium with standard atmosphere (57.5% R.H./70° F.) at the test temperature)

		Rayon			Nylon		
	Hours	Breaking strength, Kg.	Breaking extensibility, %	Hookean slope, Kg./%	Breaking strength, Kg.	Breaking extensibility, %	Hookean slope, Kg./%
Singles	0	6.15	9.6	1.57	3.91	23.5	0.16
	8	6.85	10.2	1.73	4.76	22.3	0.19
	16	6.40	10.2	1.70	4.45	22.3	0.19
	48	6.38	11.2	1.50	3.54	26.8	0.14
	120	6.26	10.4	1.67	4.48	23.2	0.16
Greige cord	0	10.42	14.0	0.86	7.42	31.6	0.19
	8	11.07	13.6	1.15	8.11	37.2	0.15
	16	10.44	14.6	1.06	8.31	35.1	0.18
	48	10.36	14.3	0.94	7.04	41.1	0.13
	120	11.35	14.2	1.23	8.19	35.6	0.18
Dipped cord	0	9.16	14.3	0.98	8.27	19.9	0.25
	8	9.80	14.3	1.05	6.82	27.1	0.19
	16	9.63	15.3	1.16	7.02	24.5	0.19
	48	9.47	12.7	1.18	8.63	20.0	0.28
	120	9.93	14.6	1.27	8.02	20.2	0.26

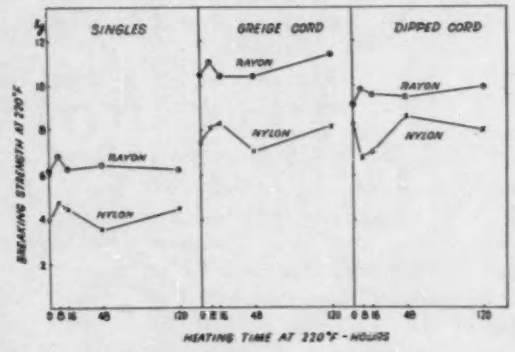


Fig. 8

at various loads. The contracting forces for the nylon cords at 220° F. and 300° F. are also evident.

Physical Properties at 220° F. After Heat Aging at 220° F.

Samples of the yarns and cords were kept in an air-circulating oven at 220° F. for periods of up to five days. They were then transferred rapidly to the hot box on the Instron tester, also at 220° F., left 10 min. to come to equilibrium, and tested under the same conditions as given previously.

Results are given in Table VII and in Figures 8, 9, and 10.

Both rayon and nylon suffered very little from this treatment. No trends could be discerned.

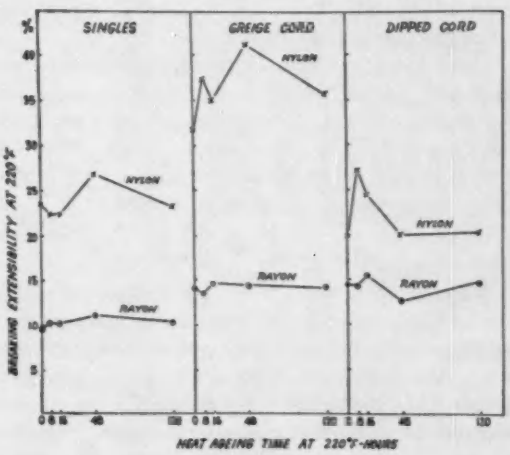


Fig. 9

Breaking strength (*Figure 8*). Essentially the same values were obtained as for instantaneous heating to 220° F. At the end of the heating period, the nylon singles, greige cord, and dipped cord respectively had only 72%, 72%, and 81% of the strength of the corresponding rayon samples.

Breaking extensibility (*Figure 9*). All samples except the nylon greige cord showed essentially the same elongation after five days at 220° F. as for instantaneous heating. At the end of the heating period the nylon extensibilities were 2.2, 2.5, and 1.4 times those of the corresponding rayon samples.

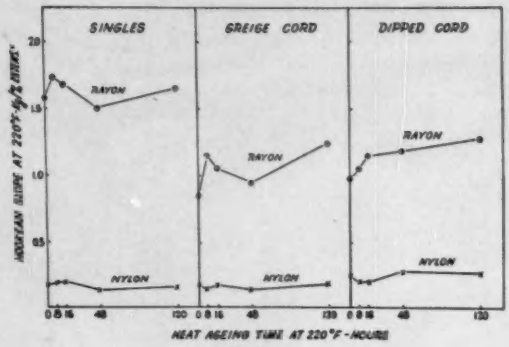


Fig. 10

The nylon extensibilities showed more variation than the rayon.

Hookean slope (*Figure 10*). The great advantage of rayon was maintained throughout the five days of heating to 220° F.

The Hookean slopes of the nylon yarn, greige cord, and dipped cord samples after five days heating were respectively only 9.6%, 14.6%, and 20.4% of the corresponding rayon samples.

Conditioned strength. It is interesting to record here that neither the nylon nor the rayon suffered any significant loss in reconditioned tests after the five days at 220° F. This and the above results for testing at 220° F. exemplify the high quality of the Canadian rayon and nylon yarns studied.

Discussion of Results

Discussion will be confined to a comparison of the dipped cords because this is the state closest to that which exists in the tire. One cannot draw hard and fast conclusions from results on a single set of samples, but the general trends seem to be in line with the behavior that might be expected from the difference in thermoelastic properties and hygroscopicity of the two fibers.

Conditioned values were preferred to anhydrous values at the lower temperatures studied because it is reported that rayon fabric in tires at normal temperature may contain 4–5% moisture [1]; this is approximately the moisture content of the dipped rayon cord under the testing conditions. This moisture will remain if the tire temperature stays down but will diffuse out at the higher temperatures.

Comparison of values per cord, and not per denier, has been adopted throughout this work, based on Mallory's statement [7] that the cost per pound, per gram per denier strength is the best criterion for determining a fiber's usefulness in tires. The rayon: nylon denier ratio of the dipped cords is 2.09:1 and the nylon:rayon price ratio is at least the same, including conversion costs, so that these two factors cancel out.

The physical test results obtained on these samples at normal temperature confirm rayon's known advantage, for tire purposes, of a higher initial modulus than nylon. This is on an equal conditioned cord strength basis, and means less growth for rayon with a static load and a smaller degree of cyclic extension with a fluctuating load. Although hot-stretching and heat-setting had reduced the ultimate extensibility of the nylon dipped cord to the same range as that of the conditioned rayon cord and had improved the Hookean slope, the latter was nevertheless still less than 50% of the value obtained for dipped rayon cord.

Increasing the testing temperature to 300° F. was advantageous for the rayon cord in comparison with nylon, in two ways. First, the ultimate breaking strength per cord became 19% greater than for nylon; second, the Hookean slope of the nylon cord fell to 30% of the rayon value.

The lowest Hookean slope of the rayon cord (at 300° F.) was considerably greater than the best value of the nylon cord (at 70° F.).

Based on this, it is believed that the rayon cords should always show less growth and a lower degree of cyclic extension than the nylon cords under the same loading conditions. The results also suggest that tires produced from the nylon cords would have to be overbuilt, strengthwise, to have the same low growth and low cyclic extension characteristics as tires produced from the rayon cords. This, of course, would add to the cost.

Literature Cited

1. Gardner, E. R. *Proc. Third Rub. Tech. Conf. Lond.*, 733 (1954).
2. Goy, R. S., *J. Textile Inst.* **48**, P637 (1957).
3. Gundavda, S. P., *J. Textile Inst.* **47**, 1298 (1956).
4. Hershey, M. P., SAE #125 "Tires for High Speed Operation," June 1957.
5. Illingworth, J. W., *Fibres* **17**, 285 (1956).
6. Illingworth, J. W. and Kilby, W. F., TEXTILE RESEARCH JOURNAL **26**, 243 (1956).
7. Mallory, G. D., TEXTILE RESEARCH JOURNAL **27**, 662 (1957).
8. Specklin, R., *Bull. Inst. Textile de France* **66**, 67 (1957).
9. Wood, J. O. and Kilby, W. F., *Proc. Third Rub. Tech. Conf. Lond.*, 711 (1954).

Non-Apparel Applications of Viscose Rayon[1]

John A. Howsmon

American Viscose Corporation, Marcus Hook, Pennsylvania

ALTHOUGH the technical history of rayon truly starts in 1891 with the discovery of the viscose reaction by Cross, Bevan, and Beadle [2], a logical industrial history begins in 1910, when Samuel Courtaulds and Co. started construction on the first viscose rayon plant in the United States. At that time, world production of viscose rayon was about 18 million pounds. In 1920, world production had increased to about 30 million pounds, of which almost one-third was made in the United States.

The next twenty years, from 1920 to 1940, could easily be called the "Golden Age" of viscose rayon. During this period world production increased sixty-five fold until in 1940 it was almost 2 billion pounds. During this period the use of rayon in apparel fields steadily increased, and in the late 1930's rayon made its first major entry into the industrial field in the form of tire yarn. During this period the major problem of the viscose rayon producer seemed to be the installation of sufficient capacity to meet the demand for the fiber. During World War II the demand for rayon for military and industrial uses grew rapidly. But even after the war, prosperity continued, until in 1951 world production reached 3 billion 300 million pounds.

In the meantime, truly synthetic fibers had appeared on the scene in 1940. They came of age about 1948, when the United States production was of the order of 70 million pounds. By the early 1950's, synthetic fiber production had reached 200 million pounds in the United States alone. The producers of rayon filament yarn and staple fiber entered what can best be stated as a period of agonizing reappraisal of their markets [1]. They were faced with the necessity of a long range reshaping of their marketing policies, as well as a long range evaluation of where their markets were and how they could be cultivated profitably.

Thus, during the "Golden Age," the rayon industry flourished under a policy which emphasized the production of large quantities of standard fibers and the selling of these standard fibers to all comers with little regard to their fitness for the intended end use. It is not surprising, therefore, that in some applications the word rayon obtained a less than palatable flavor for converters and consumers. In sharp contrast to this large volume universal fiber policy, the present rayon marketing policy can be best summarized as specific fibers for specific markets. The rayon producer has been forced to search out specific end uses in which the rayon yarns and fibers can do an attractively economic job. No market is too small or too specialized to warrant attention. It is, perhaps, noteworthy that many, if not most, of these new highly specialized end uses are in fields remote from the apparel or fashion field. Most of them are in industrial or home furnishings end uses, and many of them are hidden uses where the presence of rayon is not recognizable by the consumer. Actually, this trend toward industrial end use specialization is not new; it is merely undergoing a completely new emphasis. In the middle 1930's, almost 90% of all rayon produced went into the apparel field. In the middle 1950's only 35% was in these end uses. The remaining 65% is in sales of fiber for industrial, tire, and home furnishings use. Complete success in such a policy can occur only by abandoning the large volume universal fiber philosophy. It is contingent upon the ability of the polymer chemists and rayon technologists to alter the properties of the fiber through economic production methods to fit the needs of the end use intended. Unfortunately, commercial production of viscose rayon preceded scientific understanding of polymer processes by at least 30 years. Therefore, during the years of 1920 to 1940, when growth of the rayon industry was very rapid, technical development by present-day standards was comparatively slow. However, this period brought forth at least two technological advances which are worthy of mention.

The first of these, stretch spinning, raised viscose rayon from its early status as an artificial silk and gave it its own place in the apparel field. The major improvements, resulting from controlled stretch dur-

[1] Presented at the 27th Annual Meeting of the Textile Research Institute, New York City, March 14, 1958.

ing spinning, were increased strength and improved dimensional stability of the fiber.

The second, a chemical process modification utilizing zinc sulfate in the spinning bath, resulted in still stronger, tougher fibers and extended rayon to industrial uses, primarily as tire cord.

In the defense of the rayon technologist, it must be stated that during this period, polymer chemistry and physics and the chemistry and physics of the solid state were still a veiled mystery. It was during this period, however, that the basic research which led to the understanding of the structure and properties of polymers began. In 1913 x-ray diffraction studies gave the surprising result that cellulose was a crystalline polymer [6]. During the next thirty years crystalline structures of many polymers were evolved, and it was demonstrated that the strength of the fiber increased as the orientation of the crystalline portion of the fiber in the direction of the fiber axis increased [4, 7]. Slowly the picture evolved that the physical properties of any fiber were strong functions of the solid state structure of the polymer comprising the fiber. However, all this technology did not mature until 1941, when Nickerson [5] published a classic paper, in which he demonstrated that the crystallinity of cellulose fibers could be measured by the rate of acid attack upon the fiber. If one should be so brash as to designate a "Golden Age" of polymer and fiber technology, that age must be given as the era beginning in 1940. During this period the solid state structure of fibers and polymers was studied by many investigators. The correlation of solid state structure and the physical properties of fibers, as well as the correlation between the solid state structure and process variables in the production of the fibers, began to take form. All this work led to the firm conclusion that the structure and the properties of cellulose fibers could be varied over wide ranges by the proper control of the process variables.

Few will argue that in 1948, when synthetic fibers became of age, the properties of viscose rayon left much to be desired when compared to the properties of these newcomers. Comparison of the absolute physical properties of viscose rayon with nylon left little doubt that the tenacity of rayon was low. Manufacturers of cotton fabrics, with little rebuttal, could speak of losses in tensile strength, tear strength, wear life, and launderability when rayon was substituted for or blended with cotton. Even wool could look with pride at such properties as soil resistance and resilience.

The best property of viscose rayon appeared to be that of low price and price stability, for only when the physical properties obtained per dollar spent were compared did rayon remain competitive. However, even in those fields where value received for money spent for rayon maintained an edge, the edge was narrowing; it became obvious that in order for rayon to survive, drastic improvements in the phyical properties of viscose rayon fibers were a necessity.

During the last five years, many of the findings of research performed between 1940 and 1950 have been commercialized, and, as a result, major improvements in the physical properties of viscose rayon have been made. Initial commercial emphasis was placed on methods of improving the tensile strength of rayon so that its utility in industrial end uses could be expanded. Efforts to increase the tenacity have also resulted in improvement of other properties, such as fatigue life, wear resistance, resilience, soil resistance, and swelling.

Secondary commercial emphasis is now shifting to exploiting the improvement in these properties for specific end uses. Some of these improvements will be good enough to maintain and expand the position of rayon in certain industrial uses. Other properties will still be found wanting. However, it is not the intent to list and discuss specific end uses in which viscose rayon is presently competitive, nor to discuss those fields in which rayon needs additional major improvements, for intelligent discussion of the varied end uses in which rayon has been placed is beyond the scope of this paper. Instead, the discussion will be limited to a review of the progress in rayon technology which led to the new super rayons, and to a presentation of an up-to-date summary of their physical properties.

The viscose rayon process follows these steps: (1) reaction of alkali cellulose with carbon bisulfide to form a cellulose xanthate; (2) solution of this xanthate in aqueous sodium hydroxide (5–8%); (3) precipitation of the cellulose xanthate by the action of a bath containing sulfuric acid, a heavy metal salt (usually zinc sulfate), and an alkali metal salt (usually sodium sulfate); and (4) controlled stretching of the still swollen fibers to yield the desired orientation.

Since the spinning of rayon is a precipitation that is controlled to yield a solid that has the form and

properties of a fiber, the rules governing the precipitation of molecules should apply. However, even true molecular dispersions of cellulose xanthate must be considered as colloidal systems, because of the large molecular size and area per unit volume. The precipitation of the fiber from viscose solution by extrusion into a coagulation bath involves at least three major factors: (1) the decomposition of cellulose xanthate to cellulose by the action of acid and heat; (2) formation of insoluble heavy metal cellulose xanthates; and (3) the removal of solvent by the action of concentrated spinning baths. By controlling the relative rates of these and other variables in the process, it is possible to produce a wide range of properties in the precipitated fibers.

For example, precipitation controlled primarily by rapid decomposition of cellulose xanthate or by rapid salting out yields round fibers with relatively low tenacity and elongation. Precipitation controlled by insoluble salt formation or other interactions that delay xanthate decomposition and inhibit crystalization yields serrated fibers marked by the presence of a tough skin layer around the periphery of the fiber. These fibers generally have a higher tenacity and elongation than fibers that do not exhibit a skin effect. The difference in physical properties of these two types of fiber is illustrated in Table I; photographs of the fiber cross section are illustrated in Figure 1.

The thickness of the skin layer can be varied and is evaluated experimentally by the fact that the skin layer retains certain dyes, while these same dyes can readily be washed from the core of the fiber. According to Morehead and Sisson [3], the skin layer is formed under conditions that favor good molecular orientation and low crystallization. In any event, the entry of regenerated cellulose fibers into industrial fields was made possible by the production of these strong, tough fibers.

Prior to 1952, practically all viscose rayons exhibited the skin-core structure, as shown in the center portion of Figure 1. The development of super rayons within the last few years is a natural extension of the above processes. These new fibers are marked by a very thick skin or, in some cases, by an all skin structure (as also shown in Figure 1) and a relatively smooth cross section. They are produced by processes similar to those used in the production of the original high tenacity rayons. The new yarns have been made possible by optimizing the several process variables that favor skin formation and by the use of certain chemical additives that allow wider control of the relative rates of xanthate regeneration, zinc cellulose xanthate formation, and salting out of the polymer.

The super rayons are marked by exceptionally high tenacity, high elongation, high fatigue life, and low swelling. A comparison of the tensile properties of these fibers, and of tire cord made from them,

TABLE I. Physical Properties of Viscose Rayons

Fiber description	Tenacity, g./den.		Elongation, %	
	Wet	Dry	Wet	Dry
Round, no skin				
Low stretch	0.70	1.6	21.0	17.0
High stretch	1.3	2.0	12.0	8.0
Serrated, skin-core				
Low stretch	1.4	2.4	45.0	28.0
High stretch	2.0	3.1	23.0	18.0

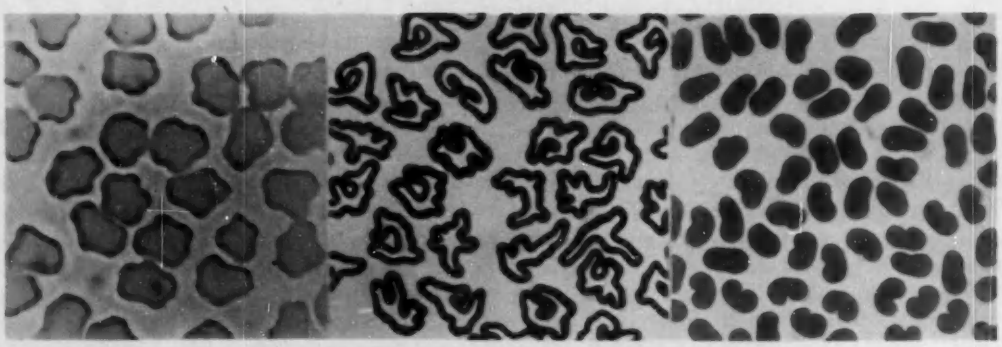


Fig. 1. Cross section photographs of three types of rayon fibers: left to right, early rayon with all-core structure; rayon with skin-core structure; and super rayon with all-skin structure.

TABLE II. Tensile Properties of High Tenacity Rayon Yarns

Year	Tenacity, g./den.		Elongation, %	
	Dry	Wet	Dry	Wet
1944	3.5	2.3	9.9	19.0
1949	4.0	2.5	10.0	21.0
1954	4.3	3.1	11.0	29.0
1956	4.5	3.3	10.5	26.0
1958	5.0	3.7	10.9	21.0

TABLE III. Tensile Properties of Rayon Cords (12 × 12 Twist)

Year	Strength, lb.	
	Conditioned	Oven dry
1944	19.0	23.5
1949	21.4	25.2
1954	25.0	29.0
1956	26.0	31.0
1958	29.0	35.0

with similar yarns having a conventional skin-core structure is given in Tables II and III. The data presented in these tables are approximate values for the high tenacity rayons commercially available in the year indicated. Data in both tables indicate that during the period from 1944 to 1949 slight improvements were made, but in general the rate of improvement was very slow.

In contrast to this, the super rayons appeared in 1952; since that time, relatively rapid improvement in the physical properties is noted. Since 1949 the strength of singles high tenacity rayon yarn has been increased by approximately 25%. At the same time, the strengths of cords produced from these yarns have increased approximately 40%. At the present time, yarn of this type has been used most extensively in tire cord, but it is well suited for, and is finding increasing use in, such diverse places as conveyor belts, V-belts, industrial sewing thread, abrasive wheels, polishing wheels, sanding disks, safety belts, packing tapes, reinforcement for paper and plastics, and even as reinforcing in plastic bearings.

There is no indication that the strength data presented here represent a ceiling for cellulose fibers of this type. It seems more reasonable that additional improvements will be forthcoming.

Initially these yarns were available only in continuous filament in tire cord deniers. However, in the last year similar yarns in the range of 600–800 den. have become available and are intended primarily for industrial uses, particularly reinforcing applications in paper, rubber, and plastics laminates. Practically all the initial applications of these fibers have been in industrial uses of continuous filament yarns. However, during this development a notable improvement in other properties was recorded, and a survey of these improvements indicated that these fibers had properties which could offer broad utility, if produced in the form of rayon staple.

In addition to higher dry and wet strength, the super rayons have high fatigue life, higher impact strength, lower swelling, are more resistant to soiling, and have higher abrasion and wear resistance than conventional rayon fibers.

Therefore, about three years ago, attention was turned to applying the principles learned in the manufacture of the high tenacity tire cord rayons to the production of staple fibers. Higher strength staple fibers began to appear. In 1957, the first commercial production of very high strength all skin staple fiber was begun; fibers of this type are now undergoing intensive trade evaluation.

The relative properties of high strength staple, conventional rayon, and cotton yarns and fabrics are given in Tables IV and V; they can be summarized as follows:

1. Yarns made from high strength staple fiber are approximately 70% stronger when wet than conventional rayon yarns and only about 15% weaker than cotton yarns.

2. High strength rayon staple yarns are approximately 40% stronger in conditioned strength than either conventional rayon or cotton yarns.

3. In comparable construction and weaves, fabrics from high strength rayon staple have 25% greater breaking strength than cotton fabrics and 30% greater breaking strength than conventional rayon fabrics.

4. In comparable construction and weaves, high strength rayon fabrics have 33% higher tear strength than cotton fabrics and 80% better tear strength than conventional rayon fabrics.

Thus, industrial and apparel fabrics made from high strength rayon staple possess significantly higher tensile and tear strengths. In addition, apparel fabrics possess firmer, fuller hand characteristics and greater covering power.

Since these properties are coupled with the necessarily higher price, it is most probable that the

largest initial end use developments will be for industrial applications where the strength characteristics can be exploited. Thus, belting and hose will gain durability with no increase in bulk. Duck fabrics for tarps and tents can be made lighter with no loss in strength. In some cases as much as 100% increase in tear strength can be realized, and it is expected that actual cost in terms of strength properties will be very competitive.

A brief summary of single fiber strengths and swelling characteristics is given in Table VI. The individual fibers of high strength staple are about 40% stronger dry and 70% stronger wet than conventional rayon, whereas there is very little difference in elongation between the two fibers. The swelling in water and the water retention are both appreciably lower than conventional rayons, but still are in the rayon rather than the cotton range. Though no data are given, the initial modulus of dry high strength rayon staple is higher than that of conventional rayon. It approaches the modulus of cotton at low extensions. (3–4%), but decreases more rapidly than that of cotton at higher extensions. The wet modulus is also slightly higher than that of conventional rayon, but the improvement is not appreciable. It should be noted, however, that in any use involving fiber blends, such properties as the low wet modulus of viscose rayon are much less important than when the fibers are used individually. In proper blends and constructions the low modulus is not a severe handicap; in fact, it closely matches those of most synthetics.

The development of the super rayons, in which the primary emphasis has been strength, is now well under way, and attention is being shifted to the exploitation of other properties and other rayons for use in fields where strength alone is not the most important factor. The most noteworthy present developments are probably in staple for carpet, nonwoven fabrics, and paper applications.

Rayon is finding wide acceptance in the rapidly growing nonwoven fabrics fields. Among the advantages of viscose rayon for use in nonwoven fabrics for laminates, plastic coating, and disposable garments, low cost, controlled length, and product uniformity are most frequently listed. To these, the property of fibrillation can now be added. Methods have been devised to produce a fibrillating rayon fiber which, when processed on conventional papermaking equipment, will produce a very high degree of hydrogen bonding. Fibrillating rayon fibers are now available for market evaluation, and it is expected that these fibers will find interesting applications in the paper and related industries.

The use of rayon staple for carpets goes back to 1950 and the advent of tufting. The early carpet fibers can now be considered merely "king size" 8.0- and 15.0-den. versions of conventional rayons of limited versatility. Steady improvement has been made in important carpet properties such as wear resistance, soil resistance, luster control, and texture

TABLE IV

	Strength, oz. to break		Elongation, %	
	Wet	Conditioned	Wet	Conditioned
Standard rayon staple	5.8	10.0	16.5	13.5
High strength rayon staple	10.1	14.6	21	18
Cotton	11.8	10.2	9	6

TABLE V. Tensile and Tear Strength of Woven Fabrics

	Tensile strength, lb.		Elmendorf tear strength, lb.
	Warp	Filling	Warp
	Standard rayon staple (68 × 72 challis)		
Conditioned	52.5	45.2	2.4
Wet	27.3	24.4	1.5
	High strength rayon staple (68 × 72 challis)		
Conditioned	67.0	56.6	4.4
Wet	39.5	37.1	3.8
	Cotton (68 × 62 challis)		
Conditioned	54.0	45.5	3.0
Wet	58.4	53.8	3.9

TABLE VI. Physical Properties of Rayon Staple (1.0 den. bright)

	Conventional	High strength
Dry tenacity	2.6	4.0
Wet tenacity	1.6	2.7
Dry elongation	24.0	22.0
Wet elongation	30.0	29.0
Cross section swelling, %	75	60
Water retention, %	95	75

potential. For example, inability to develop crimp severely limited the texture potential of the first high denier carpet staple. Newer fibers have greatly enhanced crimpability which, when combined with extreme flexibility in denier and new methods of luster control by solution dyeing and delustering, offer improved texture and "eye appeal" never before possible in carpets. In addition, special noncrimping rayon carpet fibers have been developed which outwear even crimped carpet fiber 2 : 1 and have the best soil resistance of all carpet fibers. The blending of these much sought after properties with the texture potential offered in a crimped fiber is now nearing commercial realization.

In conclusion, commercial exploitation of the super rayons is still in its infancy, and it still is too early to predict how successful they will be in expanding the position of rayon in industrial end uses. There seems no question, however, that the improved super rayons have made it possible for rayon to compete better in our industrial economy, and it is very unlikely that any new fiber will cause a major displacement of them in the near future. The present trends indicate that the synthetic fibers will continue to replace rayon fibers in some areas, but that these same synthetics will extend the use of viscose rayon fibers into other fields. The properties of cellulose and synthetic fibers complement each other to a great extent, so that the most satisfactory product for many end uses is a fiber blend to which each component contributes specific properties. A major portion of future development work in the fiber industry will be directed toward the evolution of blends embodying particular properties for specific end uses. In addition, the intelligent use of viscose rayon fibers alone in end uses specifically suited to their properties will increase their utility and allow expansion in the new fields. Continued research and application development at the producer level will result in continued improvement in the properties of the various types of rayon fibers, and the number of fiber types will increase. It will become more and more important that a fiber not be referred to simply as viscose rayon; specific reference will have to be made to the type of viscose rayon meant and the end use for which this rayon was intended. The name viscose rayon is now applied to a complete family of fibers. Most of these fibers are so different from the viscose rayons of 1940 that it is indeed doubtful that they should be called by the same name.

Literature Cited

1. Campbell, J., *Modern Textiles* **38**, 51 (September 1957).
2. Cross, C. F., Bevan, E. J., and Beadle, C., Brit. Pat. 8700 (April 8, 1893).
3. Morehead, F. F. and Sisson W. A., TEXTILE RESEARCH JOURNAL **15**, 443 (1945).
4. Morey, D. R. TEXTILE RESEARCH **5**, 483 (1935).
5. Nickerson, R. F., *Ind. Eng. Chem.* **33**, 1022 (1941).
6. Nishikawa, S. and Ono, S., *Proc. Math.-Phys. Soc. Tokyo*, **7**, 131 (1913).
7. Sisson, W. A., TEXTILE RESEARCH **7**, 425 (1937).

Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

An Application of the Davidson Color Matching Method

Department of History and Philosophy of Science
University of Melbourne
Australia
May 6, 1958

To The Editor

TEXTILE RESEARCH JOURNAL

Dear Sir:

An ingenious solution to the 'artificial light' color matching problem in the dyeing of textiles was proposed by Davidson [1], using spectrophotometric data for each component in a mixture of dyes. Because problems associated with color matching are similar in both fabric dyeing and paper printing, an attempt was made to apply the Davidson procedure in the latter field. This note records some typical preliminary results which suggest the possibility of extensive application. The method resolves into the use of the formula

$$F_M = \frac{a}{A} F_1 + \frac{b}{B} F_2 + \cdots + F_0\left(1 - \frac{a}{A} - \frac{b}{B} - \cdots\right) \quad (1)$$

where $F = (1-R)^2/2R$, R being the reflectance of the surface at a given wavelength (subscripts M, 1, 2, 3 . . . refer respectively to a mixture and its components). F_0 is a correction factor for the undyed base material and is a term of such low value that it can be neglected except for measurements on very light colors.

$A, B, C \ldots$ denote the concentrations for which the spectrophotometric curves of components 1, 2, 3 . . . were obtained.

$a, b, c \ldots$ denote the respective concentrations of components 1, 2, 3 . . . in the mixture M.

Experimental

All reflectance measurements were performed on ink draw-downs made on the smooth side of strips of a lightweight machine-grained lithographic paper. The draw-downs were made using a constant volume of applied ink (to give a spot of approximately 2.0 cm. diameter) and a knife with which to spread the ink into an elongated ellipse of approximately 5.0 cm. maximum width and 35 cm. length. This constancy of the applied volumes of inks (with equal solids contents) spread over approximately equal areas of paper justified the assumption that the concentrations of colored components (i.e., $A, B, C \ldots$) were constant for each draw-down.

Reflectances (R) were determined with a Photovolt Photoelectric Reflection Meter No. 610 according to the standard procedure as recommended by the manufacturers.

F values were taken from a standard table [1].

Results and Discussion

With a draw-down technique as described, the actual values of $A, B, C \ldots$ are not readily determined. However, because of similar solids contents of the inks used, $A, B, C \ldots$ can be considered to be constant (assumed equal to 100). Thus in a three-

TABLE I. *F* Values of Unknown Colors

Filter wavelength (*A*)	F_{M1}	F_{M2}
444	1.44	5.29
576	2.91	2.21
607	2.64	1.13
632	2.21	0.48
670	2.21	0.54

TABLE II. *F* Values of Suggested Components

Filter wavelength (*A*)	Mixture *M*1		Mixture *M*2		
	F_1	F_2	F_1	F_2	F_3
444	2.21	0.03	4.60	4.93	4.31
576	3.60	0.02	1.60	1.29	1.73
607	3.60	0.01	0.77	0.45	4.05
632	2.91	0.01	0.18	0.12	3.23
670	3.06	0.01	0.20	0.16	3.60

TABLE III. *F* Values of Calculated Mixtures

Filter wavelength (*A*)	F_{M1}	F_{M2}
444	1.54	5.29
576	2.91	2.21
607	2.64	1.29
632	2.21	0.57
670	2.21	0.54

component mixture, the desired concentrations (wt./wt.) to be determined (i.e., *a*, *b*, *c*) are expressed directly as percentages. Hence

$$A = B = C = a + b + c = 100 \qquad (2)$$

For a three-component mixture, from Equations 1 and 2,

$$100\,F_M = aF_1 + bF_2 + cF_3 \qquad (3)$$

Similarly, for a two-component mixture,

$$100\,F_M = aF_1 + bF_2 \qquad (4)$$

In two typical examples *M*1 and *M*2, the printed samples whose colors were to be matched gave *F* values at five wavelengths as set out in Table I.

Practical consideration of a number of factors, such as the surface to be printed, the method of printing, and the properties of the various inks, suggested that the desired unknown colors *M*1 and *M*2 could be attained by use of two- $(F_1 + F_2)$ and three- (F_1, F_2, F_3) component mixtures respectively. Reflectances of draw-downs of all such suggested components were measured at five wavelengths and converted to *F* values (Table II).

To solve for *a*, *b*, and *c* in the *M*2 mixture (likewise in the simpler two-component mixture *M*1), appropriate substitution of *F* values in Equation 3 gives five equations, any pair of which, with Equation 2, will provide by standard mathematical operations the values of the unknown quantities.

By solving

$$0.18a + 0.12b + 3.23c = 48$$
$$0.20a + 0.16b + 3.60c = 54$$
$$a + b + c = 100$$
$$a = 67 \quad b = 21 \quad c = 12$$

Similarly for *M*1

$$a = 74 \quad b = 26$$

Synthetic mixtures were made according to these percentages and their *F* values determined as previously (Table III). Such values show very close agreement with those of the unknown samples (Table I) and, as would be expected, prints using inks prepared with the calculated composition were acceptable visual matches.

Literature Cited

1. Davidson, H. R., *Am. Dyestuff Reptr.* **41**, 1 (1952).

F. BRYANT

Isolation and Identification of Fumaric Acid in Raw Cotton Fiber

Crops Research Division
Agricultural Research Service
U. S. Department of Agriculture
Beltsville, Maryland
June 10, 1958

To the Editor

TEXTILE RESEARCH JOURNAL

Dear Sir:

The organic acid content of raw cotton fiber has been studied by various investigators [5, 6, 7, 8]. They have reported the presence of malic, citric, and oxalic acids in the fiber. McCall and Guthrie [6] give the average organic acid composition of four cotton varieties as 0.46% malic acid, 0.06% citric acid, 0.004% oxalic acid, and 0.31% unidentified organic acids, for a total of 0.84% organic acids. The unidentified organic acids, in this as in other cotton analyses, constitute a high percent of the total acids in the fiber. In re-examining the chemical composition of the cotton fiber in this laboratory, fumaric acid has been found to be one of the components of the acid fraction. Its isolation and identification are reported here.

Unweathered cotton fiber from the following varieties was used: Deltapine 15 and a double haploid Deltapine, both grown in the greenhouse at Beltsville; field grown Coker 100 Wilt from Florence, South Carolina; and field grown Acala 4-42 from Shafter, California. In all four varieties fumaric acid was found to be present.

A 2-g. sample of each variety was extracted with boiling 80% ethyl alcohol. The alcohol was evaporated to near dryness in a rotary evaporator below 40° C. and the residue taken up in water. Following centrifugation of the extract, the cleared supernatant was passed through a 10 cm. × 0.5 cm.² column of Amberlite I R A 400 (formate form), adapted from the procedure of Bryant and Overell [2]. The column was first washed with water; then the organic acids were eluted from the column with 45 ml. of 6 *N* formic acid. The formic acid was evaporated to dryness in a rotary evaporator below 40° C. and the nonvolatile organic acids examined by paper chromatography.

The three solvent systems used were:

System 1 [9]: Ethyl ether—5 vol.; 85–90% formic acid—2 vol.; water—1 vol.

System 2 [1]: Ethyl alcohol—90 vol.; ammonium hydroxide—5 vol.; water—5 vol.

System 3 [2]: Mesityl oxide—75 vol.; 85–90% formic acid—36 vol.; water—75 vol.

With the first two systems, the ascending method was used. A descending method [4], modified for organic acids, was used for the third system. Solutions of the acids were spotted on Whatman #1 filter paper. In System 3 the paper was equilibrated for 2–4 hr. with the aqueous phase of the solvent. A filter paper circle with 4-stranded wick, 2 in. long, was used for controlling the solvent flow. After the paper was dried free of all solvent, it was rolled in brom-phenol blue indicator [9]. The acids appear as yellow spots on a blue background.

The chromatograms showed three distinct spots, with R_fs identical to those given by the standard solutions of citric, malic, and fumaric acids chromatographed on the same paper. In some of the chromatograms, a spot appeared between citric acid and the origin; the identity of the substance is yet to be determined.

The R_{malic}s of the acids in the different solvent systems are presented in Table I. The acids from all four varieties gave identical R_fs.

For the isolation of fumaric acid, the gradient elution technique of Bush, Hurlbert, and Potter [3] for separation of the tricarboxylic acids, using ion-exchange resins, was used, with the modifications introduced by Palmer [9]. Since there is so much malic acid in the cotton fiber, it was desirable to separate it from the rest of the acids in the isolation procedure. This allowed the concentration of a relatively large amount of fumaric acid in a small column, thus facilitating the isolation of the acid in sufficient amounts to carry out identification tests. A sample (100 g.) of field grown unweathered Acala 4-42 cotton fiber was extracted three times with boiling 80% ethyl alcohol. After the alcohol was evaporated off, the residue was taken up in water. The solution, cleared by centrifugation, was passed through a 10 cm. × 0.78 cm.² Dowex 1-X10 (200–400 mesh, formate form) column. The organic acids were eluted from the column (6 *N* formic acid in the reservoir); 40 fractions of 3 ml. each were collected

TABLE I. R_{malic}s* of the Nonvolatile Organic Acids From Raw Cotton Fiber

Acid	Ether system		Mesityl oxide		Ammonia system	
	Fiber	Standard	Fiber	Standard	Fiber	Standard
Citric	.83	.84	.80	.83	.08	.08
Malic	1.00	1.00	1.00	1.00	1.00	1.00
Fumaric	1.59	1.59	2.04	2.02	2.00	2.00

* Since malic acid has been identified as the major organic acid in the cotton fiber, it was used as the reference compound.

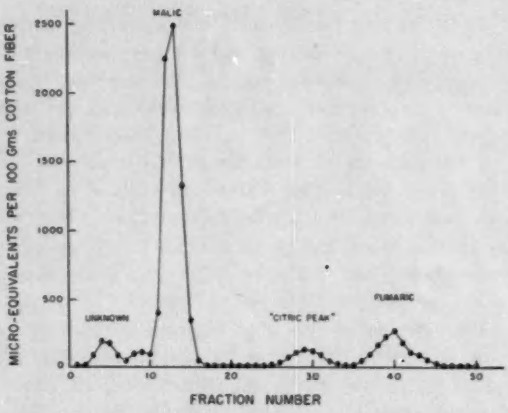


Fig. 1. Elution diagram for the anion fraction of Coker 100 Wilt unweathered cotton fiber. Dowex 1-X10 (200–400 mesh, formate form) 4 cm. × 0.28 cm.² column. Gradient elution, with 6 *N* formic acid in reservoir. Flow rate, 1 ml./min.; fraction volume, 3 ml. Data in terms of micro-equivalents per 100 g. dry fiber.

after the first 60 ml. of eluate (mainly malic acid) was discarded. The formic acid was evaporated and each fraction was examined by paper chromatography (Solvent System 1); those showing fumaric acid were combined. The pooled fractions were then passed through an 8 cm. × 0.28 cm.² Dowex 1-X10 (200–400 mesh, formate form) column, and elution was performed with 6 *N* formic acid in the reservoir. After the first 50 ml. of eluate had been discarded, 40 fractions of 3 ml. each were collected. The fractions were chromatographed again to check for citric acid contamination. Fumaric acid appeared free of contamination in fractions 10 to 22 inclusive. The acid emerged from the column after citric, in about the same fraction position as Palmer [9] found for fumaric using pure organic acids.

The formic acid was evaporated from each of the above 13 tubes. The white powdery residues were then bulked and weighed; 100 g. of cotton was found to yield 56 mg. of fumaric acid. The acid was then transferred to a 10-ml. centrifuge tube, dissolved in boiling water, and allowed to crystallize at room temperature. The crystals were washed twice with cold water and dried over P_2O_5.

A sealed-tube melting point of 280° C. was obtained with the crystals, compared to 285° C. for the authentic acid.

The purified acid, authentic fumaric acid, and a mixture of the two were chromatographed; identical R_f values were obtained.

It may be seen in Figure 1 that the fumaric acid peak appears in the same sequence as in Palmer's elution diagram [9] for the ion exchange separation of pure organic acids.

Calculations from the curve in Figure 1 indicate that on a dry weight basis this particular sample contained approximately 0.5% malic acid, 0.05% citric acid, and 0.07% fumaric acid, plus 0.60 meq. of unknown acid. Further study is in progress to elucidate the qualitative aspect of the unknown organic acid peak.

Literature Cited

1. Brown, F., *Nature* **167**, 441 (1951).
2. Bryant, F. and Overell, B. T., *Biochim. et Biophys. Acta* **10**, 471 (1953).
3. Bush, H., Hurlbert, R. B., and Potter, V. R., *J. Biol. Chem.* **196**, 717 (1952).
4. Irreverre, F. and Martin, W., *Anal. Chem.* **26**, 357 (1954).
5. Kursanov, A. T. and Vyskrebentseva, E. F., *Biokhimiya* **17**, 480 (1953).
6. McCall, E. R. and Guthrie, J. D., *J. Am. Chem. Soc.* **67**, 2220 (1945).
7. McCall, E. R. and Jurgens, J. F., TEXTILE RESEARCH JOURNAL **21**, 19 (1951).
8. McCall, E. R., Cirino, V. O., Stark, S. M., and Guthrie, J. D., *Science* **108**, 360 (1948).
9. Palmer, J. K., *Agr. Exp. Sta. Bull.* 589 (1955).

LUIS E. GREGORY [1]
GEORGE V. MEROLA

[1] Present address: Territorial Experiment Stations Division, Federal Experiment Station in Puerto Rico, Mayaguez, Puerto Rico.

Improvement on the Servo Conversion of Manual Fibrographs

Southern Utilization Research
and Development Division
1100 Robert E. Lee Boulevard
New Orleans, Louisiana
April 18, 1958

To the Editor

TEXTILE RESEARCH JOURNAL

Dear Sir:

In 1952, a simple servo system was described [3] and illustrated [4] for converting manual models of the Fibrograph to automatic operation. A number of instruments are known to have been converted and are still in operation.

Further improvement in performance can be obtained by the additional modifications described below, which will permit stable operation with full servo amplifier gain. The result is greater accuracy of trace and higher speeds of operation. These suggested modifications in no way alter the basic features of the instrument or the results obtained with it.

Analysis of the Fibrograph amplifier [1] indicates that the desired signal, i.e., the unbalance between the cotton and standard photocells, is essentially D.C. in character. However, there is also present a strong A.C. signal due to the excitation of the fluorescent and incandescent lamps.

Adequate filtering may be accomplished by removing the front panel and connecting a condenser from ground to the grid supplied by the photocells. This is pin No. 4 of the 6SC7 tube in the schematic wiring diagram shown in the Operating Instructions [1]. The value of the condenser is not critical, but due to space limitations a 0.05-mfd. 600-volt condenser is suggested. Insertion of this condenser allows removal of the filtering and divider network at the input of the servo amplifier [3].

Unless the servo amplifier used is of unusually high amplification, it may be desirable to increase the amplification in the Fibrograph itself. This will reduce the dead zone [2] and is very simply done by connecting an additional resistor between the cathode of the 6SC7 (pin No. 6) and ground. The values are not critical. An 82,000-ohm 0.5-watt resistor has been used in the instrument at this laboratory.

Although addition of the condenser removed the A.C. signal as a source of "blocking," large changes in unbalance such as are encountered when the fluorescent lamp holder is lifted may cause temporary blocking at the high amplification. To eliminate this a simple "clamp" consisting of two germanium diodes such as the type 1N34 are connected in parallel but with opposite polarities; that is, with the positive end of one diode fastened to the negative end of the other, and *vice versa*. The parallel diodes are connected directly across the servo amplifier input, which is connected to the Fibrograph without any further input network. The "clamp" limits the input signal when it is excessive but due to the non-linearity of the diodes it has no appreciable effect for small signals.

Literature Cited

1. Fulton-Sylphon Division, Robertshaw Controls Co., Operating Instructions for Model 800-F Fibrograph. Knoxville, Tennessee (1948).
2. Gibson, V. D. and Terry, R. A., *Characteristics of the Brown Electronik Continuous Balance System.* Minneapolis-Honeywell Regulator Co., Philadelphia, Pa., Bull. 12–15 (1950).
3. Tallant, J. D., TEXTILE RESEARCH JOURNAL **22**, 617–619 (1952).
4. Tallant, J. D., *Textile World* **103**, No. 2, 107 (1953).

JOHN D. TALLANT

Book Reviews

The Technology of Cordage Fibers and Rope. David Himmelfarb. New York, Interscience Publishers, 1957.

Reviewed by Stuart J. Hayes, Ludlow Manufacturing and Sales Co., Needham Heights, Mass.

This excellent book about cordage fibers is slanted towards rope making, but it discusses basic principals of chemistry, physics, and engineering that apply to the modern techniques of all the bast and leaf fiber products. To cover a very wide field within the limits of one modest volume, some chapters are condensed almost to oversimplification. Hence, while the work is not a primer and while beginners may find it difficult to follow, any reader with moderate facility in textile engineering will find it a delight to peruse, and the expert will welcome it as a reference source.

The text does not pretend to be original research. The concepts presented are up to date, and data are drawn from sources not commonly available. The conclusions and comments reflect the author's wide technical and practical experience. Statements are illustrated by numerous well chosen tables, and opinions are bolstered by ample documentation.

The early chapters summarize the botany, chemistry, physics, and microscopy of the bast and leaf fibers and some man-made fibers. Fiber preparation, the physics and geometry of spinning for three quite different fiber types, rope making, and finishing operations are described in detail. Much of the discussion of problems essential to rope making is equally valid for makers of yarns and threads.

The physical properties of rope (but equally well of any twisted product) are presented as the combined influences of geometry upon forces of torsion, bending, tension, and shear. The effects of moisture, swelling, and rates of load upon strength are discussed. It is noted that rope uses only 50–75% of the inherent strength of the yarns, and yarn in turn utilizes only a modicum of the fiber strength. Elongation, elasticity, and creep are differentiated. Relations between twist angle and twist balance are explored. The forces exerted during a knot break are analyzed. The relative efficiency of several standard knots is tabulated. Endurance of fibers under several conditions of abrasion and bending is compared.

Protection of fiber products against chemical and biological damage and weathering are explained. Chemical damage usually means acid damage or oxidation, and might result from paint, oils, free mineral acid, and some organic solvents. Man-made and natural fibers are both subject to damage, but by different classes of reagents. The normal reaction of bast and leaf fiber is correctly given as 5.0–7.0 (not ph 7.0 as has been appearing recently in commercial specifications).

Weathering depreciation is variable; moreover, the correlation between instruments purporting to simulate accelerated weathering and results from exposure to outdoor weather is notoriously poor. The only dependable estimate of weather resistance is exposure on outdoor racks.

Storage deterioration seems to be unavoidable. Even under model conditions, the degradation would vary from 1% to 10% annually, and average about 2.0%.

Microbial damage is amply canvassed. Fungicides are explored. An excellent table shows the degree of inhibition of 16 commonly used fungicides. Treatment with even dilute concentrations of a dependable fungicide is considered a sound insurance investment for cordage. Suggestions are given for the care and handling of ropes to prolong their useful life.

The book concludes with a welcome list, briefly describing by their commercial names all or nearly all the known types of cables, cords, falls, halyards, hawsers, lines, ropes, twines, and yarns. Generic specifications are tabulated for the principal items. Specialists may find minor errors; nevertheless the list is the only authoritative compilation now in print. A well organized index closes the book.

The book repeatedly gives the critical comment of the expert, balancing the technical limitations of available machinery against inherent fiber characteristics, making allowances for what practically can be accomplished within the existing framework of costs, space, and personnel. This weighing of theory

against practice lifts the book from a compilation of data to an authoritative text.

Mr. Himmelfarb has made a commendable addition to textile literature.

Rheology: Theory and Applications. Volume I. F. R. Eirich, Ed. New York, Academic Press, Inc., 1956. xiv + 761 pages. Price $20.00.

Reviewed by Joseph H. Dusenbury, Textile Research Institute, Princeton, New Jersey

This volume is the first of a three-volume series dealing with the science of the deformation and flow of matter. It is the apparent purpose of this series to demonstrate and present a unified treatment of the diverse topics that have been considered to come under the general heading of rheology. There is a very brief introduction by Professor Eirich; this is followed by 16 other chapters on various topics and of varying length. Following these chapters, there is an appendix which contains a brief survey of Weissenberg's general theory of deformation. The author and subject indices at the end of the book appear quite comprehensive and add to the value of the book.

The problem of mathematical symbols in the case of this book is a difficult one, and, in this reviewer's opinion, it has been handled in the best way possible at this time. There really is no set of agreed-upon standardized symbols in the rheology field at present, although efforts are underway in this direction. Under these circumstances, the provision of a list of symbols for each chapter appears to be a good compromise and has been made here.

No attempt will be made here to review all portions of this work. The variety of topics is so great that a report on each would cause this review to be excessively long. Such a review would also be presumptuous on the part of the reviewer, for he is not familiar with all of the areas covered in this treatment of rheology. In those areas where this reviewer felt more at home, the topics have been discussed in a competent and thorough fashion. In particular, the chapter by Professor Reiner on "Phenomenological Macrorheology," which includes a discussion of the Weissenberg effect, the chapter on "Theories of Viscosity" by Bondi, the chapter on "Large Elastic Deformations" by Rivlin, the chapter on "Dynamics of Viscoelastic Behavior" by Alfrey and Gurnee, and the chapter on "Streaming and Stress Birefringence" by Peterlin all proved to be instructive and interesting. It should be noted here that in most of these chapters, as well as in the others on such topics as plasticity and hardening of metals, dislocation theory, and acoustical methods of testing, the treatment is often highly mathematical, and tensor theory is used frequently.

Unfortunately, in the chapter by Peterlin, Dr. Treloar's name is misspelled in each place where it appears, whether in text or in footnote. Other than this difficulty, the entire work seems to be remarkably free of error. The figures and tables appear to have been selected carefully and are instructive. The book is well printed, and the format is attractive. If the prices of the next two volumes are as high as for this one, however, it is doubtful whether many rheologists will feel they can afford their own copies.

In the Preface, Professor Eirich states, "Thus it is hoped that this book will be instrumental in bringing about a better understanding of the essential unity of rheology." This work should go far towards achieving the benefits that would come from such an understanding.

Conference on Military Applications of Fabrics for Coating

Natick, Massachusetts

October 16–17, 1958

A conference on military applications of fabrics for coatings will be held at the Quartermaster Research and Engineering Center, Natick, Massachusetts, October 16 and 17, 1958, under the sponsorship of the Textile Fabrics Committee, Quartermaster Advisory Board, National Research Council, National Academy of Sciences. The program is listed below; for further information, please contact Dr. W. George Parks, Quartermaster Advisory Board, National Research Council, National Academy of Sciences, Washington, D. C.

Tentative Program

1. Military Applications for Coated Fabrics
   - Dr. S. J. Kennedy — Quartermaster Research & Engineering Center, Natick, Mass.
   - Mr. R. Grubb — Philadelphia Naval Shipyard
   - Mr. J. H. Ross — Wright Air Development Center, United States Air Force

2. Design for Climatic Extremes
   - Dr. Austin Henschel — Quartermaster Research & Engineering Center, Natick, Mass.

3. Interaction of Fabric Structure and Coating Type as Affecting Performance
   - Dr. M. M. Platt — Fabric Research Laboratories

4. Fabrics for Coating: Design and Construction
   - Mr. W. Corey — The Landers Corp., Toledo, Ohio

5. New Fibers and Yarns for Coated Fabrics
   - Mr. R. C. Pike — Textile Fibers Department, E. I. du Pont de Nemours & Co., Inc.

6. Technical Advancement in Coating Materials for Fabrics
   - Mr. F. H. Fritz — Elastomer Chemicals Department, E. I. du Pont de Nemours & Co., Inc.

7. Evaluation of End Item Performance
   - Mr. K. L. Keene — United States Rubber Company, Mishawaka, Indiana

8. Coating Technique
   (Speaker to be Named)